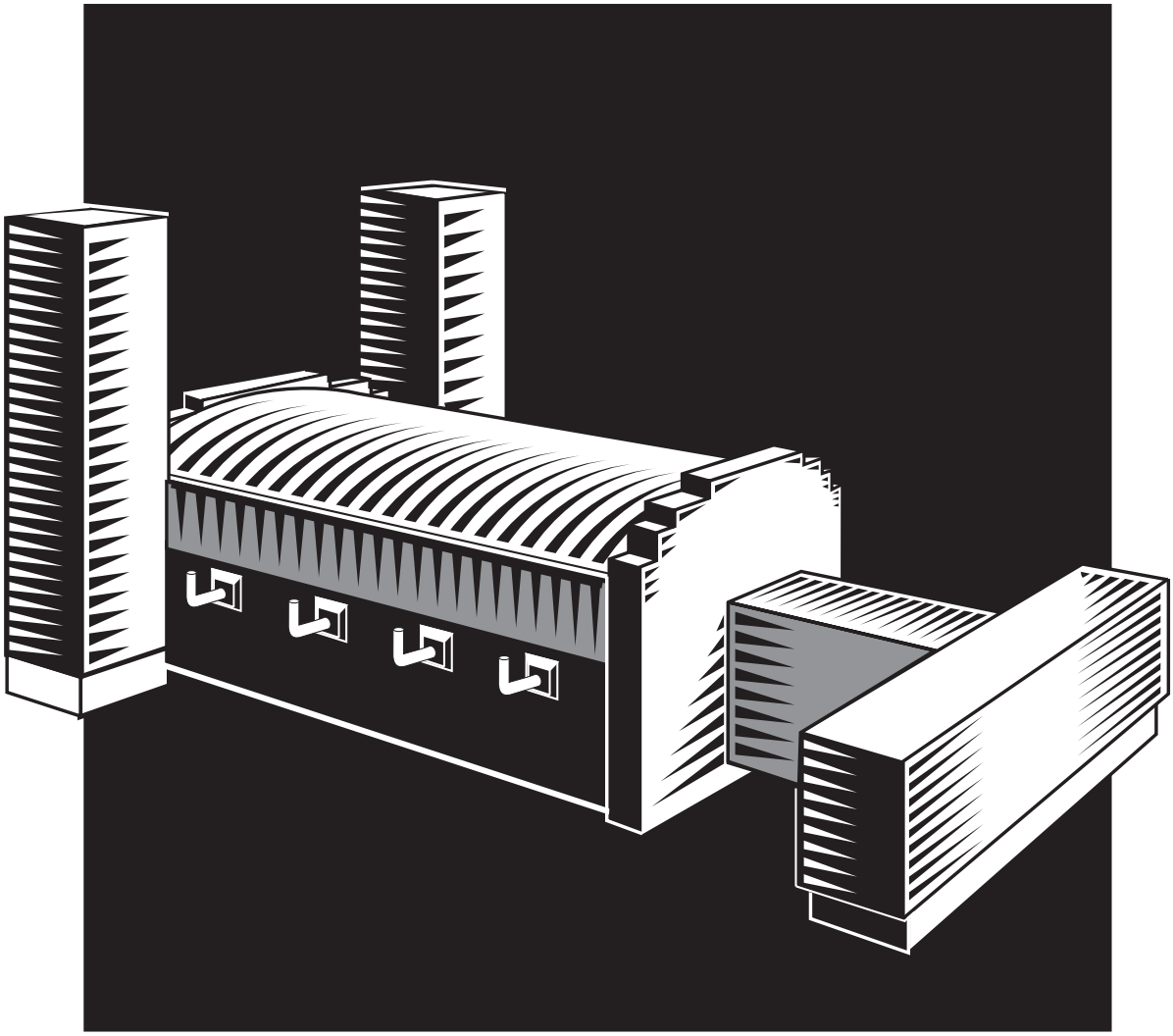
Glass Industry of the Future

Quarterly Status Reports

As of September 30, 2002



U.S. DEPARTMENT OF ENERGY

02-GA50113-03

Glass Industries of The Future Quarterly Reports Received for September 30, 2002

Production Efficiency

1. PNNL: Advanced Process Control for Glass Production (1009)
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2. PNNL: Auto Glass Process Control (807)
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3. SNL (PPG): Development of Models and On-Line Diagnostic Monitors of the High-Temperature Corrosion of Refractories in Oxy/Fuel Glass Furnaces (1012 & 1021)
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4. NETL: Enhanced Cutting and Finishing of Handglass Using a Carbon Dioxide Laser (1024)
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5. Energy Research Company: Measurement and Control of Glass Feedstocks (1609)
   Arel Weisberg
   aweisberg@erco.com
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6. Alfred University: Modeling of Glass Making Processes for Improved Efficiency (718)
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7. State of Ohio: Improvement of Performance and Yield of Glass Fiber Drawing Technology
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Energy Efficiency

8. ANL: Development and Validation of a Coupled Combustion Space/Glass Bath Furnace Simulation (Techneglas) (1025)

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9. SNL: Glass Furnace Combustion and Melting Research Facility (1022)

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Environmental

10. ANL: Development of a Process for the In-House Recovery and Recycling of Glass Manufacturing Wastes (1611)

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11. SNL/Gallo Glass Company: Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulates and Crown Corrosion (1608)

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Innovative Uses

12. Alfred University: Integrated Ion Exchange for High Strength Glass Products (1030)

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13. PPG Industries, Inc.: Development of Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Flat Glass (1640)

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Acknowledgement:
The Glass Manufacturing Industry Council (Cooperative Agreement No. DE-FC07-02ID14318, OITIS# 1034)) is instrumental in coordinating with contractors and providing the quarterly reports on their web site. The Glass Manufacturing Industry Council (GMIC) has accomplished a number of significant milestones towards the ultimate goal of reaching a long-term "Vision" objectives.

Production Efficiency

PNNL: Advanced Process Control for Glass Production

Quarterly Progress Report

Project Title: Advanced Process Control for Glass Manufacture

Covering Period: Jul. 1, 2002 to Sept. 30, 2002

Date of Report: Nov. 15, 2002

Laboratory: Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99353

FWP/OTIS Number:

Subcontractors: None

Other Partners: Thomson Multimedia

Contact: Chester Shepard; (509) 375-3675; chester.shepard@pnl.gov
Moe Khaleel; (509) 375-2438; moe.khaleel@pnl.gov

Project Team: Elliot Levine, DOE; Mel Ehrlich, Thomson Multimedia

Project Objective:

The production of formed glass products is an energy intensive process. This project is aimed at enabling a process control system for the manufacture of television glass products. The research and development team includes personnel from Pacific Northwest National Laboratory (PNNL) and Thomson Consumer Electronics. Process control first requires knowledge of the relationships between plant operational parameters and the physical properties of the resulting glass product. Thompson has extensive archived data from which these relationships can be established. We will perform multi-variate testing of the Thomson plant data for development of the backbone of a process control system. Process control also requires the availability of adequate modeling of the glass forming process as well as advanced sensor data to provide critical physical parameters. In this project we will perform work to advance modeling capabilities as well as develop novel sensors for physical measurements. Glass modeling will focus on the formation of glass in molds. The models will be based on finite element codes and will include radiation as an integral part of heat transfer. Advanced sensors include an optical instrument for measurement of residual stress throughout the thickness of a glass article and an optical instrument for 3D measurement of glass temperature.

Background:

Glass manufacture, regardless of the industry involved, consumes large amounts of energy and produces significant amounts of atmospheric pollutants. This project will support improved production efficiency of television glass articles and thereby enable reduction of plant emissions and energy usage. Energy savings and pollution reduction will result from reduced reprocessing of glass parts. In addition, significant time and labor savings will follow from the efficient process design capability and yield improvements. Improved process control allows the replacement of iterative control methods used in many glass manufacturing plants.

This project will address quality control for mold-formed and heat treated TV glass components (i.e. dimensions and internal stress distributions). We will utilize several tools to help achieve these goals. First, we will perform multi-variate testing of archived Thomson plant data to quantitatively establish the relationship between plant operational parameters and the physical properties of the glass product. In addition, we will continue the development of non-contact three dimensional stress and temperature measurements and improved simulation tools (coupled to finite element codes) for the design of optimized glass production.

Thomson Consumer Electronics is collaborating with PNNL in support of the activities described in this proposal. Thomson produces the front glass panels for television sets. Many companies are investing in the development efforts to enable improved process and quality control for a wide variety of glass products.

The improved non-contact stress and temperature measurement capability will enable similar quality control in many glass industries, ranging from automotive to architectural applications where the glass must meet structural and strength criteria. The numerical models developed in this project will be applicable to a host of problems including dynamic fluid flow and forming of sheet metal components within dyes. Applicability simply requires replacement of constitutive models which describe the material behavior. The process control software is also widely applicable to other glass production processes since these operations essentially involve the same steps.

Work performed over the previous periods has resulted in a novel method for measurement of stress in TV glass and for measurement of temperature. A patent application will be submitted for the stress measurement method. Modeling studies have now been advanced to the point where FEA codes can be used for modeling of the glass cooling stages that follow formation.

Status:

Work performed over the past quarter has focused primarily on one task: model development. Model development has advanced significantly. Full quarter-symmetry finite element code calculations for a TV panel have been performed using the MARC code coupled to the PNNL radiation transport code. Results obtained with these coupled codes have been compared with results obtained when using an effective thermal conductivity for heat transport. The PNNL heat transport code has been shown to run extremely fast and can operate on a PC.

The stress measurement task was largely completed during a previous reporting period and only modest efforts were expended during this period. A report has been submitted to Thomson Multimedia outlining experimental results obtained with their glass samples. A manuscript has been submitted to the Journal of the American Ceramic Society for publication. This manuscript has now been accepted for publication and should be in print sometime during CY03. The results of this experimental work have been excellent and a very powerful method for measurement of stress throughout the entire glass thickness has been developed.

Project results were presented at the annual Glass Project Review Meeting held at Livermore CA on September 10, 2002.

No problems have been recorded in regards to milestones or schedule.

Plans for Next Quarter:

There are no plans for the next quarter. This project is complete.

Patents:

No patents have yet resulted from this work. However, an invention disclosure for the measurement of stress has been submitted and it is expected that a patent application will be filed before the end of the fiscal year.

Publications/Presentations:

A presentation was made during the annual DOE-OIT Glass Project Review meeting held at Livermore CA this year. Due to its length and the fact that the presentation has already been made available to the DOE in electronic form, this presentation is not included here. An article has been submitted and accepted for publication as described above.

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Glass Forming Simulation	4/1/02	8/30/02	Work completed
2	Glass-Mold Interaction Simulation	5/1/02	8/30/02	Work completed
3	Multi-Variate Analysis of Plant Data	9/1/02	8/30/02	Work completed
4	Demonstrate Optical Stress Sensor	6/1/02	5/1/02	Work completed
5	Demonstrate Optical Temp Sensor	7/1/02	9/1/01	Work completed

Budget Data (as of date): Sept. 30, 2002

Phase/Budget Period			Approved Spending Plan			Actual Spent to date		
	From	To	Doe Amount	Cost Share	Total	DOE Amount	Cost Share	Total
Year 1 (proj 29569)	7/99	9/99	$266	$0	$266	$78	$0	$78
Year 2 (proj 29569)	10/99	9/00	$184	$110	$294	$211	$110	$321
Year 3 (proj 29569)	10/00	9/01	$301	$165	$466	$403	$165	$568
Year 4 (proj 29569 & 43752)	10/01	12/02	$220	$180	$400	$259	$180	$439
Totals			$971	$455	$1,426	$951	$455	$1,406

PNNL: Auto Glass Process Control

Quarterly Progress Report

Project Title: Auto Glass Process Control

Covering Period: Jul.1, 2002 to Sept. 30, 2002

Date of Report: Nov.15, 2002

Laboratory: Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99353

FWP/OTIS Number:

Subcontractors: None

Other Partners: Visteon Glass Division (Mike Brennan), PPG (Rick Reuter)

Contact: Moe Khaleel; (509) 375-2438; moe.khaleel@pnl.gov

Other PNNL Contacts: Ken Johnson, (509) 375-2241; Vladimir Korelev, (509) 372-4082; Chester Shepard, (509) 375-3765

Project Team: Elliot Levine, DOE;

Project Objective:

Automotive glass manufacture is the largest per-vehicle energy consumption process step in vehicle production and produces significant amounts of atmospheric pollutants. The proposed project will support improved production of sheet, formed, and heat-treated glass parts to enable reduction of vehicle weight and energy use and pollution emissions. Component weight reduction will be enabled by the use of more uniform glass parts. Energy use reduction and pollutant emission reduction will result from reduced reprocessing of unacceptable glass parts. In addition, significant time and labor savings will result from the efficient process design capability and yield improvements in the production process. Specifically, this will allow the replacement of the current iterative methods used to finalize the glass quenching equipment and process design, which can cost up to $250K for each new windshield design.

This project will address improved properties and quality control for formed and heat treated glass components (i.e., dimensions and internal stress distributions) which will result from the development of non-contact three dimensional stress and temperature measurement methods and improved simulation tools for the design of optimized glass treatment processes.

Background:

Automotive glass manufacture is the largest per-vehicle energy consumption process step in vehicle production and produces significant amounts of atmospheric pollutants. The proposed project will support improved production of sheet, formed, and heat-treated glass parts to enable reduction of vehicle weight and energy use and pollution emissions. Component weight reduction will be enabled by the use of more uniform glass parts. Energy use reduction and pollutant emission reduction will result from reduced reprocessing of unacceptable glass parts. In addition, significant time and labor savings will result from the efficient process design capability and yield improvements in the production process. Specifically, this will allow the replacement of the current iterative methods used to finalize the glass quenching equipment and process design which can cost up to $250K for each new windshield design.

This project will address improved properties and quality control for formed and heat treated glass components (i.e., dimensions and internal stress distributions) which will result from the development of non-contact three dimensional stress and temperature measurement methods and improved simulation tools for the design of optimized glass treatment processes. The automotive industry is currently making significant investments related to the needs targeted in the PNNL proposal.

Visteon Automotive Systems is collaborating with PNNL in support of the activities described in this proposal. Ford and many companies are investing in the development efforts to enable improved process and quality control for automotive glass.

The improved non-contact stress and temperature measurement capability will enable similar component weight and pollution emission reductions for many other glass applications including architectural applications where the glass must meet structural and strength criteria to ensure that installed glass will survive the range of anticipated stresses. The cooling and solidification of casting and tempering of metal components will benefit from the stress measurement and modeling methods that are developed. The numerical models used in this project will work equally well for the forming of sheet metal against a die with the replacement of a constitutive model that describes the metal behavior.

Past work done over several years has resulted in the demonstration of two new methods for the measurement of stress and temperature in auto glass. Two patent applications have been filed. The numerical code RAD3D for calculation of the radiative contribution to temperature has been completed and integrated with commercial finite element codes.

Status:

Work performed over the past quarter has focused primarily on further development and refinement of the RAD3D code. Code features that have been completed include internal radiation calculations, multiple glass layer capability, surface emissivity variation, view factor calculations, and multiple and time varying source/sink temperatures. The RAD3D code has been coupled to the MARC code. Proper handling of boundary conditions and verification of useful calculational approximations are issues that were solved during the past quarter.

Modeling of glass forming in the PPG single zone furnace has commenced and some results are now at hand. Problems that have been modeled with the PPG furnace include single and double layer glass and layered glass with a coating between the layers. Model results are in close agreement with measurements obtained in experiments with the furnace. Deep gravity sag formation of windshields within the PPG furnace has been modeled using the Marc code.

No problems have been recorded in regards to milestones or schedule.

Plans for Next Quarter:

Plans for next quarter involve continuation of the work performed over the past three quarters. Sample problems from industrial partners will be modeled with the help of the RAD3D code coupled to the Marc code.

Patents:

Two patent applications have been filed:

1. System and method for glass processing and stress measurement, by BD Cannon, CL Shepard, and MA Khaleel. Filed July 24, 2001.
2. System and method for glass processing and temperature sensing, by CL Shepard, BD Cannon, and MA Khaleel. Filed May 15, 2001.

Publications/Presentations:

Four publications have resulted from this work.

1. MA Khaleel, JL Woods, and CL Shepard, *Glass Technology*, **42**, 49-53, April 2001.
2. CL Shepard, BD Cannon, and MA Khaleel, *Int. J. of Heat and Mass Transfer*, **44**, 4027-4034, Aug. 2001.
3. BD Cannon, CL Shepard, and MA Khaleel*, Applied Optics*, **40**, 5354-5369, Oct., 2001.
4. MA Khaleel, CL Shepard, and BD Cannon, *Ceramic Industry*, **151**, 52-55, Oct.,2001.

A presentation was made during the annual DOE-OIT Glass Project Review meeting held at Livermore, CA on Sept. 10, 2002. Due to its length and the fact that the presentation has already been made available to the DOE in electronic form, this presentation is not included here.

Milestone Status Table:

ID Number	MILESTONE	PLANNED Completion	Actual Completion	Comments
1.1	Demonstrate double thermal grating approach for stress measurement	2nd Q 1999	2nd Q 1999	
1.2	Demonstrate first prototype stress measurement system	4th Q 1999	4th Q 1999	
2.1	Demonstrate through thickness optical temperature measurement	2nd Q 1999	2nd Q 1999	
2.2	Demonstrate first prototype optical temperature measurement system	4th Q 1999	4th Q 1999	
3.1	Finalize process optimizations using 3D coupled numerical models	3rd Q 2000	3rd Q 2000	
1.3	Validated stress measurement technique	3rd Q 2000	3rd Q 2000	
1.4	Complete final prototype optical systems for measurement of stress and temperature	3rd Q 2000	3rd Q 2000	
1.5	Automate our stress measurement technique	4th Q 2000	4th Q 2000	
1.6	Extend stress measurement to low stress	1st Q 2001	1st Q 2001	
1.7	Improve automated polarization analyzer	1st Q 2001	1st Q 2001	
2.3	Improve measurement resolution for temperature above 500ºC	1st Q 2001	1st Q 2001	
3.2	Provide industrial partner with the modeling code and documentation	2nd Q 2001	2nd Q 2001	
3.3	Deliver final report marking completion of project	2nd Q 2001	2nd Q 2001	
4.1	Host Glass Program Review Meeting	4th Q 2001	4th Q 2001	
1.8	Extend code capability to cover multiple absorption spectrums	2nd Q 2002	2nd Q 2002	Completed
1.9	Develop code and provide documentation and manuals to partner	4th Q 2002	4th Q 2002	Progress on schedule

Budget Data (as of date): 9/30/02

Phase/Budget period			Approved Spending Plan			Actual Spent to Date		
	From	To	DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
Year 1(Proj 26099)	10/97	9/98	$271	$265	$536	$265	$265	$530
Year 2(proj 26099)	10/98	9/99	$340	$300	$640	$317	$300	$617
Year 3(proj 26099)	10/99	9/00	$150	$150	$300	$140	$150	$290
Year 4(proj 26099)	10/00	9/01	$116	$100	$216	$101	$100	$201
Year 5(proj 26099)	10/01	9/02	$150	$150	$300	$101	$100	$201
Totals			$1,027	$965	$1,992	$924	$915	$1,839

SNL (PPG): Development of Models and On-Line Diagnostic Monitors of the High-Temperature Corrosion of Refractories in Oxy/Fuel Glass Furnaces

Quarterly Report

Title	Development of Models and On-Line Diagnostic Monitors of the High-Temperature Corrosion of Refractories in Oxy/Fuel Glass Furnaces
Project Period	July 1, 2002 – September 30, 2002
Laboratory	Sandia National Laboratories Mail Stop 9052 Livermore, CA 94551-0969
B&R No.	NM269020000
FWP/OTIS Number:	EEW234
Contact:	Mark D. Allendorf (925)294-2895 mdallen@sandia.gov

Project Team:

Industrial Partners:	Air Liquide, BOC Gases, Gallo Glass, PPG Industries
Subcontractors	Prof. Karl Spear (Pennsylvania State University) Prof. Mariano Velez (University of Missouri, Rolla) Monofrax Inc. (Dr. Amul Gupta) RHI Refractories (Dr. Tomas Richter)

Project Objectives

This research is directed toward understanding the mechanism(s) of enhanced refractory corrosion in oxy/fuel glass furnaces and the development of models to predict corrosion rates, identify operating regimes that minimize corrosion, and define the attributes of improved refractories.

The project has three objectives: First, the factors controlling the rate of refractory corrosion in glass furnaces will be identified through a combination of experiments in controlled laboratory environments and characterization of corroded samples using sophisticated analytical techniques. Second, this knowledge will be used to develop, validate, and exercise one or more models that can predict corrosion rates as a function of refractory properties (chemical and structural) and furnace conditions. Third, since knowledge of gas-phase alkali concentrations (particularly NaOH and KOH) will almost certainly be essential to developing strategies for minimizing corrosion in a specific furnace, laser-based detection methods will be explored to serve as an on-line process monitor of these species.

Background:

Conventional glass melting furnaces using combustion of natural gas or oil with air typically employ bonded silica refractory brick to construct the furnace superstructures. In a well-

designed, properly insulated and sealed, and well-operated furnace, silica refractory structures will last at least 10 years in a float furnace, and slightly less in container-, specialty- and insulating-fiberglass furnaces. Under certain conditions, however, it can be significantly attacked by alkali vapors, such as sodium hydroxide (NaOH), that volatilize from the glass and by airborne batch particles, producing defects in the glass and shortening crown life by as much as a factor of two to three. The mechanisms for the enhanced corrosion of refractories in oxy/fuel furnaces are not completely clear, although the composition of the furnace gas and the temperature profile across the refractory are expected to be important factors. Gas-phase alkali species (such as sodium hydroxide or potassium hydroxide), in conjunction with water vapor, are the most likely compounds that attack the refractory, although lead used to make television glasses and boron used to make fiberglass may also be factors. It appears that an understanding of at least five factors must be obtained in order to identify the important corrosion mechanisms: 1) the identity and concentration of gas-phase species at the refractory surface; 2) the rates of transport of these species to the surface and through either the porous refractory or cracks/joints between bricks; 3) the temperature profile across the brick; 4) the rates of chemical reactions occurring at the surface and within the capillaries of the brick; and 5) the rate of transport of liquid corrosion products to and away from the brick surface.

Status:

Task 1 Experimental characterization of corrosion processes

- Task complete.

Task 2 Corrosion modeling

- A first-generation software module was provided to to Air Liquide for incorporation in their *Athena* furnace code. The module simulates front-face corrosion of silica, using the analytical model and thermochemistry developed earlier in the project. Preliminary simulations of the Gallo Tank 1 furnace have been conducted.

Task 3 On-line monitors for gas-phase alkali detection

- Completed a series of LIFF response calibrations such that the beta –alumina electrode data from the Rolla group could be directly compared with the LIFF data recorded during the 12/01 field tests. This enables us to express our measured LIFF signal as an absolute NaOH concentration in ppm. Results showed that during batch operations at Rolla, the transient (~ 1 minute) NaOH concentrations were as high as 250 ppm.

- Brought the LIFF instrument to the PPG plant in Fresno and assembled it inside the furnace building. Coordinated with Mr. Greg Rolio and Mr. Richard Hernandez at PPG. Assembly went well, but the testing encountered an electronics failure in a high voltage pulse generator, resulting in no LIFF measurements in the furnace. Several Important lessons were learned: 1) the detector cooling water that is available at the plant is too hot; 2) additional modifications of air conditioning ducting will help cool the instrument head better; 3) no other significant logistical challenges to the field tests exist.

- Worked directly with G. Pecoraro (PPG) at Fresno, operating PPG's direct atmospheric sampling apparatus. With this "hands-on" training, S. Rice (SNL) will be able to

conduct both LIFF and direct sampling measurements simultaneously at a number of ports on the Fresno plant furnace during the next field test.

- Repaired the LIFF instrument and scheduled a return to Fresno for the week of 12/02/02.

Plans for Next Quarter:

- Provide data concerning measured NaOH concentrations to Air Liquide to allow them to modify their NaOH vaporization subroutine.
- Complete initial CFD modeling of crown corrosion in Gallo Tank 1 using the modified NaOH vaporization in conjunction with the Sandia corrosion model.
- Repeat field test at PPG Fresno facility.

Patents: None this reporting period.

Publications and Presentations:

M. D. Allendorf "Development of Models and On-Line Diagnostic Monitors of the High-Temperature Corrosion of Refractories in Oxy/Fuel Glass Furnaces," OIT Glass Program Review Meeting, Sept. 10, 2002, Livermore, CA.

Milestone Status

The project is currently in Phase III/Year 1 (Year 4) of the project. The status of individual tasks is given in the table below.

Task	Task/Milestone Description	Completion Date		Comments
		Plann	Actual	
1.1	Compile corrosion database	3/00	3/00	
1.2	Corrosion experiments, silica	9/00	9/01	
2.1	Build mathematical models	9/00	3/01	
2.2	Compile thermodynamic data	3/99	9/99	
2.3	Equilibrium modeling	9/99	3/00	
2.4	Validate model performance	9/00	12/00	
2.5	Develop analytical submodels	9/02	6/30	
2.6	Design user interfaces	4/03		
3.1	LIFF furnace measurements	9/00	9/00	
3.2	Lab-scale furnace tests	9/00	12/01	
3.3	Design/fab portable system	6/01	9/01	
3.4	Field test 1	3/01	12/01	
3.5	Field test 2	9/01		new date 12/02
3.6	Field test 3	9/02		new date 3/03

Budget Data

			Approved Spending Plan			Actual Spent to Date		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	10/98	9/99	260	170	430	260	170	430
Year 2	10/99	9/00	325	175	500	325	175	500
Year 3	10/00	9/01	375	120	495	375	120	495
Year 4	10/01	9/02	250*	60	310	200	138**	338
year 5	10/02	9/03	200	60	260			
		Totals	1,410	585	1,995	1160	603	1,733

*FY02 (Year 4) request is $250 K. To date (4/30/02) $200 K has been allocated.
**Includes carryover from FY01.

NETL: Enhanced Cutting and Finishing of Handglass Using a Carbon Dioxide Laser

4

A quarterly report for this project was not received by the report cut-off date of November 27, 2002.

Energy Research Company: Measurement and Control of Glass Feedstocks

5

QUARTERLY PROGRESS REPORT

Project Title: Measurement and Control of Glass Feedstocks

Covering Period: July 1, 2002 through September 30, 2002

Date of Report: October 15, 2002

Recipient: Energy Research Company

Award Number: DE-FC07-01ID14030

Subcontractors: Oak Ridge National Laboratory

Other Partners: PPG Industries
Fenton Art Glass

Contact(s): Arel Weisberg, Ph.D.
(718) 608-0935
aweisberg@er-co.com

Project Team: DOE-HQ Contact: Elliot Levine
Contract Specialists: Matea McCray, Layne Isom, Joseph Keller

Project Objective: Energy Research Company (ERCo) is developing an on-line sensor for controlling the quality of glass feedstocks, both batch and cullet. In the case of batch, the sensor can determine whether or not the batch was formulated accurately, and serve as part of a feedback loop in the plant to control glass quality. In the case of cullet feedstocks, the sensor can serve as part of a system to sort cullet by color and ensure that it is free of contaminants.

Background: The Glass Industry Technology Roadmap[1] emphasizes the need for accurate process and feedstock sensors. Listed first under technological barriers to increased production efficiency is the "Inability to accurately measure and control the production process." ERCo's LIBS sensor addresses this need by giving plant operators critical knowledge of their batch composition. In plants where cullet is used in glass production, the LIBS sensor can provide color sorted cullet free of contaminants, including those contaminants that are not detectable using current optical based color sorters.

[1] Available at: http://www.oit.doe.gov/glass/pdfs/glass2002roadmap.pdf

LIBS utilizes a highly concentrated laser pulse to rapidly vaporize and ionize a small amount of the material being studied. As the resulting plasma cools it radiates light at specific wavelengths corresponding to the elemental constituents (e.g. silicon, aluminum, iron) of the material. The strengths of the emissions correlate to the concentrations of each of the elemental constituents. This technology has been successfully demonstrated in ERCo's LIBS laboratory for both batch analysis and cullet sorting. In the upcoming year, designs of prototype sensors for installation at the program's industrial partners will be developed.

Status:

1. **Executive Summary**

The current quarter's activities included expanded cullet tests and the first quantitative tests of batch materials. In addition, representatives from ERCo presented the results of this program at the OIT Glass program review at Sandia National Laboratory.

This quarter concluded 18 months of effort into developing the glass feedstock sensors, and the program is currently on schedule.

2. **Initial Quantitative Batch Measurements**

PPG Fiberglass provided ERCo with samples of clay, silica, limestone, colemanite, and ulexite powders that are typical of those used in production. In addition to these samples, PPG also provided ERCo with fiberglass buttons (i.e. small disks) from their Shelby, NC plant for testing. PPG also provided the elemental composition of the button, as measured in the Shelby plant laboratory. The clay powder was sent to an independent laboratory for measurement of it's silicon, aluminum, iron, and titanium concentrations.

The clay and button samples were analyzed in ERCo's LIBS facility. The clay was rotated on a turntable beneath the laser pulse so that each laser pulse sparked new material. The level of the clay surface was kept constant with a plastic "wiper" that swept the clay surface to a fixed height just before the laser pulse.

Spectra from 25 consecutive laser pulses were averaged together to produce a single spectrum for analysis from the clay. Five of these average spectra were analyzed from each of the two clay samples. ERCo's calibrationless LIBS software was used to determine the clay's elemental concentrations. This software, being developed by ERCo, is unique in that it does not utilize calibration curves to convert LIBS spectra into concentration meaurements. The main benefit of this approach is that periodic recalibrations would not be required in a commercial installation.

The results from the analysis are shown below in Table 1. Only the percentage error is reported because the actual concentrations are confidential PPG data.

Table 1: Results from Calibrationless Analysis of PPG Clay Samples

Element	Sample 1 Mean Error (%)	Sample 2 Mean Error (%)	Signal-to-Noise
Aluminum	2.0	1.9	Good
Silicon	1.8	2.3	Good
Titanium	2.8	6.9	Good
Iron	8.5	13.5	Poor

The accuracy of the results of this test tracks with the concentration of the elements. Silica and alumina are the most abundant elements, and the accuracy of their measurement is best. Titanium and iron are present in substantially lower amounts, which is reflected in the less accurate results. We will be improving the algorithm over the coming months to overcome as much of this effect as possible.

The fiberglass button was also analyzed in the ERCo LIBS facility. The button was sparked by the laser 20 times at 20 different locations on the button's surface, and the resulting spectra were averaged together. This average spectrum was analyzed with ERCo's calibrationless software. The results are shown in Table 2. As in the case of the clay, only the percentage error is reported because the actual concentrations are confidential PPG data.

Table 2: Results from Calibrationless Analysis of PPG Fiberglass Button

Element	Error (%)	Element	Error %
Aluminum	2.9	**Boron**	22.4
Silicon	1.7	**Sodium**	3.3
Titanium	15.0	**Magnesium**	3.1
Iron	4.7	**Calcium**	6.1

The large errors in the titanium and boron are unusual in this case since their concentrations are not small. We will investigate the reasons for this result in the upcoming months.

Overall these results are promising. Consequently, we are continuing to develop and refine the calibrationless LIBS algorithm.

3. Expanded Cullet Tests

Cullet sorting tests were expanded in this quarter to include 12,000 spectra from 25 samples, including 6 contaminants. As in previous tests, the cullet samples were placed on a turntable and rotated beneath the laser pulse in order to simulate cullet flowing in a commercial sorter. Rotation rates corresponding to cullet velocities in a commercial sorter were used. A photograph of a LIBS spark on cullet rotating on the turntable is seen in Figure 1.

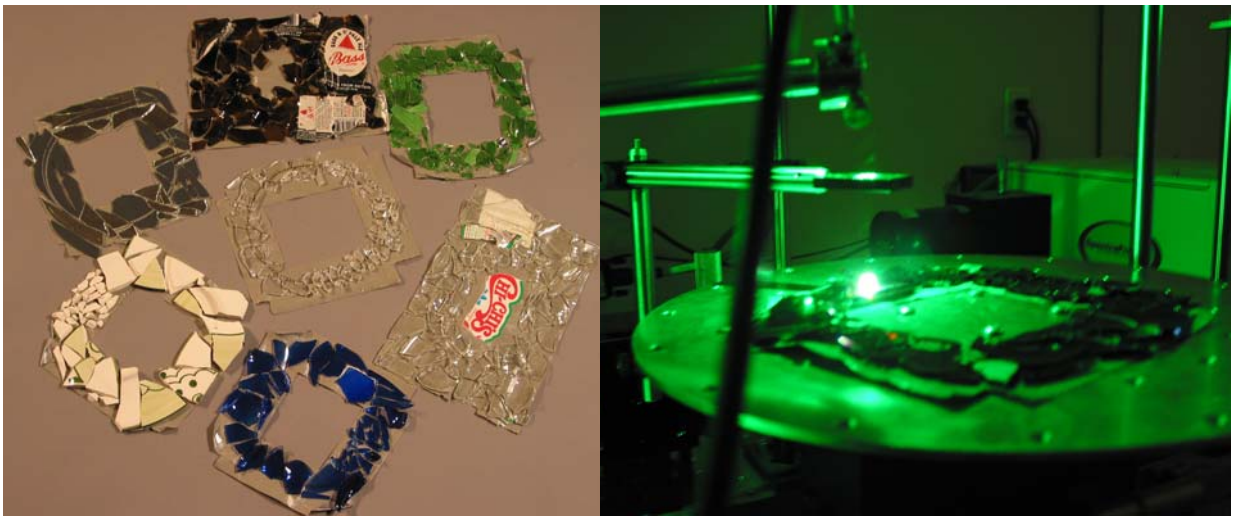

Figure 1: Samples of Cullet and Contaminants (right) and a Photograph of a LIBS Spark on Rotating Cullet (left)

In addition to increasing the number of cullet samples, the sorting software was rewritten to more closely simulate a commercial sorting device. LIBS typically employs a spectrometer for measuring the plasma emission. However, spectrometers are too slow for commercial cullet sorting in which hundreds of spectra, corresponding to hundreds of cullet pieces, must be analyzed each second. Therefore, in a commercial cullet sorter single channel silicon detectors would be used. These detectors are fast enough for analyzing cullet at rates of hundreds per second because they only measure one narrow wavelength, as opposed to the hundreds or thousands measured by spectrometers.

However, because the spectrometer would be replaced by several detectors, the amount of spectral data available to the sorting algorithm is vastly reduced. This fact greatly increases the degree of difficulty in identifying each piece of cullet.

The cullet sorting algorithm was revised to simulate the silicon detectors based system. In this series of tests a spectrometer gathered the LIBS data but only data corresponding to wavelengths that would be gathered by the detectors was analyzed.

The results of the test are summarized in Table 3. Given the increased difficulty in sorting cullet using detectors, these results are highly encouraging.

Table 3: Summary of Cullet Sorting Test with Silicon Detector Simulation

Color / Contaminant	% Correct Identification
Flint	97.5
Green	95.3
Amber	90.8
Contaminants	98.5

4. Presentation at OIT Glass Program Review Meeting

In September, ERCo representative presented the results of the prior year's effort at the annual review meeting. Cheryl Richards of PPG also aided in the presentation. Discussions with other glass researchers and glass company representatives were also very useful, as was their feedback on ERCo's efforts.

Plans for Next Quarter:

During the next quarter we will focus on refining the batch constituent measurements, both through more traditinal methods that rely upon calibration data, as well as through further development of the calibrationless method.

A visit to Fenton Art Glass is also scheduled for November to discuss installation of a LIBS batch sensor in Year 3 of the program.

Patents: N/A

Publications/Presentations:

See attached presentation from the review meeting.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Laboratory Development			
1.1	Facility Modification	9/30/01	9/30/01	
1.2	Testing	3/31/02	2/28/02	
1.3	Initial Software Development	3/31/02	3/31/02	
1.4	Performance Evaluation	3/31/02	3/31/02	
2	Sensor Fabrication			
2.1	Facility Construction	9/30/02	8/31/02	
2.2	LIBS Testing	3/31/03		
2.3	Software Development	3/31/03		

Budget Data (as of 9/30/02):

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	4/01	12/01	423,178	181,501	604,679	47,184		47,184
Year 2	1/02	12/02	509,525	710,613	1,220,138	141,287	196,951	338,238
Year 3	1/03	12/03	506,110	717,688	1,223,798	19,156		19,156
Year 4								
Year 5								
		Totals	1,438,813	1,609,802	3,048,615	207,627	196,951	404,578

Alfred University: Modeling of Glass Making Processes for Improved Efficiency

Project Title: Modeling of Glass Making Processes for Improved Efficiency
(Subtitled: High Temperature Glass Melt Property Database for Modeling)

Covering Period: July 1, 2002 through September 30, 2002

Date of Report: October 25, 2002

Recipient: New York State College of Ceramics at Alfred University
2 Pine Street
Alfred, NY 14802

Award Number: DE-FG07-96EE41262

Subcontractors: CELS at Corning Incorporated, Corning, NY
Laboratory of Glass Properties, St. Petersburg, Russia
Pacific Northwest National Laboratories, Richland, WA

Other Partners: NSF Industry/University Center for Glass Research at Alfred University

Contact(s): Principal Investigator - Thomas P. Seward III
Telephone: 607-871-2432
E-mail: seward@alfred,edu

Other investigators – Alexis G. Clare, David A. Earl, William C. LaCourse, Dolun Oksoy, James E. Shelby, Arun K. Varshneya and Terese Vascott (all at Alfred University), Oleg A. Prokhorenko (at the Laboratory of Glass Properties, St. Petersburg, Russia) and Pavel Hrma (at Pacific Northwest National Laboratories)

Project Team: DOE-OIT Glass Team Leader – Elliott Levine
DOE Program Manager –Elliott Levine
DOE Project Manager – Matae H. McCray
Grant Administrator – Marshall Garr
Industry Contact – Industrial Liaison Board of the NSF Industry/University Center for Glass Research at Alfred University

Project Objective:

To develop a high-temperature melt properties database with sufficient reliability to allow mathematical modeling of glass melting and forming processes. The commercial glass families chosen for investigation are float, container (soda-lime-silica), low expansion borosilicate, color television panel, insulation wool and E-type textile fiber glasses. Properties of primary interest

include gas solubility and diffusivity, density, thermal expansion, surface tension, viscosity, electrical conductivity and radiative thermal conductivity.

Background:

Glass manufacturing is a capital-intensive industry. In 1996, the cost of a new float glass facility was estimated to be about $150 million. The corresponding figures for fiberglass, container glass and color TV tube bulbs were $80, $100 and $300 million, respectively [1]. Furnace rebuilding costs run into millions of dollars. It is imperative that any proposed changes in furnace design have near 100% assurance of success. Lost production resulting from a poor furnace design can ultimately cost far more than the construction. Radical changes in design are almost always considered “high risk.” On the positive side, design improvements, which improve production yields or result in even a 5% decrease in fuel consumption per ton of glass melted, would have important economic and environmental benefits for the industry. Consequently modeling of the glass-melting process to predict performance has become a necessity for any new furnace design.

In July 1996, the U.S. Department of Energy (DOE) and the NSF Industry/University Center for Glass Research (CGR) conducted a workshop at Alfred University on “Modeling in the Glass Industry.” Two of the primary needs identified for virtually all modeling of the glass melting process are 1) reliable data on high-temperature melt properties and 2) improved sensors for in-line measurement of process variables. Also deemed important is an “improved understanding” of the fundamental principles of combustion and the fluid flow models themselves.

This project addresses the need for reliable high-temperature melt property data.

[1] P. Sewell. “Industrial Perspective of Modeling in a Modern Float Glass Plant,” *the GlassResearcher* **6** [2] 1-3 (1997)

Status:

1. Executive Summary

Melting of all required glasses was completed this quarter and viscosity measurements continued throughout the quarter. The high temperature rotating spindle viscosity measurements are now being conducted at PNNL using G-PLUS funding (Schott Glass Technologies 2002). The low temperature (parallel plate) viscosity measurements are continuing at Alfred with only nine glasses remaining to be measured. Additional funding was awarded by the DOE to help complete all measurements by year-end 2002.

2. Glass Melting and Analysis

All remaining fiberglass wool and soda-lime-silica (container and float) compositions were melted at Alfred this quarter by post-doctoral researcher Alex Fluegel. The soda-lime-silica

glasses will be sent elsewhere for chemical analysis, as will the wool glasses if sufficient funding remains.

3. Gas Solubility and Diffusivity (J.E. Shelby, PI)

3.1 Solubility (CGR-funded)

As previously reported, this work is essentially complete, except for argon.

3.2 Diffusivity (J.E. Shelby, PI)

As previously reported, water diffusivity measurements for all six base glasses* is complete.

* "Base glasses" means the commercial glasses supplied to this project by CGR member companies. They are considered typical of their families and provide the basis for the systematic composition variations studied in this project.

4. Density, Thermal Expansion and Surface Tension (A.G. Clare, PI)

Measurements are complete on five of the six commercial base glasses.

5. Viscosity (A.G. Clare, J.E. Shelby, A.K. Varshneya, PIs)

The viscosity range of interest spans 10^1 to 10^{14} Poise (1 to 10^{13} Pa.S). No single technique is capable of measuring over this range. Hence, we are employing three techniques:

5.1. Rotating spindle viscosity measurements (10^1 - 10^4 Poise) - Measurements are complete for all six base glasses and nearly complete for several of the sets of composition variations. As stated in the Executive Summary, the remaining measurements are now being conducted at PNNL using Schott Glass Technologies, Inc. 2002 G-PLUS funding. We have received an additional award from the DOE, about $10,000 of which will go directly to PNNL to enable the completion of these measurements. We anticipate that work will be complete by the end of October.

5.2. Parallel plate viscosity measurements (~ 10^5 - 10^9 Poise) – Alex Fluegel, a post-doctoral researcher reporting to Dr. Arun Varshneya, was employed (using CGR/NYSCC related funds) from January 2002 through August 2002. He completed the required measurements on all but about nine glasses. We should be able to obtain the remaining measurements by the end of November.

5.3. Beam bending viscosity measurements (~ 10^{10} - 10^{13} Poise) – This portion of the work was conducted during 2001 under the direction of Dr. Jim Shelby and funded by the CGR. Measurements are complete for 13 container, 10 float, 23 E-glasses, 25 low-expansion borosilicate glasses, 14 wool glasses, and 25 TV panel glasses, i.e., all the glasses that were available at that time. An undergraduate student is measuring the remaining glasses this fall.

5.4. Non-Newtonian viscosity (at viscosities near 10^{11} Poise)

As previously reported, work in this area is complete.

6. High Temperature Radiative Conductivity (O.A. Prokhorenko, PI)

As previously reported, work in this area is complete.

7. Electrical Resistivity (T.P. Seward and A.K. Varshneya, PIs)

Measurements on all six commercial base glasses and almost all available experimental glasses were completed by December 2001. This fall, the CGR Assistant Director of Technology, Terese Vascott, is performing measurements of the most recently melted glasses.

8. Oxygen Partial pressure (Redox) (T.P. Seward, PI)

The redox state of the low-expansion borosilicate commercial glass still needs to be measured.

9. Glass Physical Properties (J.E. Shelby, PI)

About two years ago, Dr. James Shelby and several of his students undertook to measure important glass physical properties on all the available glasses, using supplemental funding from the CGR. These properties include density, refractive index, coefficient of thermal expansion, dilatometric softening point, glass transition temperature, dissolved water concentration and electrical conductivity at 200˚C and 300˚C. The properties were measured on all of the glasses available through the end of 2001. Properties of the remaining glasses will be measured this fall, to the extent that funding is available under this project.

10. Statistical Analysis of Data (D. Oksoy, D. Earl, PIs)

Last year (2001) Dr. David Earl and his graduate research assistant, Rebecca Neill, completed the statistical analysis of the available electrical resistivity data for the full set of TV panel glasses. The data was fitted to Arrhenius plots with only 3 out of 360 data points being statistical outliers. This analysis phase stopped in May (2002) when Rebecca's funding ran out.

Dr. Dolun Oksoy will begin the statistical analysis of the viscosity data as soon as a full set of data is available for any one of the glass families.

11. Evaluation of Data by Member Companies

No change from last quarter.

Plans for Next Quarter:

Plans for next quarter include completing the electrical resistivity and parallel plate viscosity measurements at Alfred and the rotating spindle viscosity measurements at PNNL. Chemical analysis of the remaining glasses will be started.

Patents: None

Publications/Presentations:

A formal review of this project was presented to representatives of the DOE Office of Industrial Technologies and GMIC (the Glass Manufacturing Industry Council) in Livermore, CA, September 9, 2002.

For the PI's perspective on the gas solubility, gas diffusivity, density, surface tension and radiative thermal conductivity studies performed in conjunction with this award, please see:

T.P. Seward III, "Aspects of the Glass Melt Properties Database Investigations at Alfred University," 61st Conference on Glass Problems, C.H. Drummond, ed., American Ceramic Society, Westerville, OH, (2001) 149-163.

Milestone Status Table: This should be a complete list of project milestones, anticipated completion dates and actual completion dates. The milestone identification number should correspond to the task numbers in your agreement to aid in tracking (example below).

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
Phase I	Designate systems to be measured, purchase and set up equipment, implement quality assurance program, calibrate equipment, train personnel, evaluate experimental procedures, implement industry suggestions, prepare glass samples, start data collection, write semiannual research reports.	12/97	12/98	Chemical analysis of all glass samples was added to the project task list. With the exception of melting/preparing some remaining glass samples and completing chemical analysis of three glass families, this phase is essentially complete.

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
Phase II	Complete data collection for all but visco-elastic properties, gas solubility and thermal diffusivity, analyze data, complete glass sample preparation, start data transfer to the industry, evaluate data, implement industry suggestions, maintain quality assurance program, write annual and semiannual research reports.	12/98	Ongoing	Thermal diffusivity was abandoned. Data collection is still in process. Data analysis started. Data transfer to industry started through the CGR members Web site.
Phase III	Complete data collection, complete data analysis, transfer data to industry, evaluate data, implement industry suggestions, collect data for any special compositions that are necessary, write annual and semiannual research reports	12/99	Ongoing	No-cost extension granted until 12/31/02. Increased funding of $18,000 has been requested from the DOE to allow completion of the glass melting and chemical analysis and the viscosity measurements at PNNL.

Note: The explanation we offered the DOE for the additional time requested to complete this project was that the original proposal underestimated 1) the amount of time it would take to complete the work using student labor, 2) the difficulties that would be encountered melting/making the required quality and quantities of glass and 3) the difficulties that would be encountered with the calibration, standardization and maintenance of several key pieces of measurement equipment.

Budget Data (as of 3/31/02): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods.

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To					$200K	$200K
Year 1	9/96	9/97	$468K	0	$468K	$229K	23K	252K

Year 2	10/97	9/98	320K	0	320K	412K	172K	584K
Year 3	10/98	9/99	200K	0	200K	318K	109K	427K
Year 4	10/99	9/00	200K	0	200K	177K	176K	353K
Year 5	10/00	9/01	318K	0	318K	232K	150K	382K
Year 6	10/01	9/02	0	0	0	119K	39K	158K
Year 7	10/02	12/02	7K	0	7K			
		Totals	1,513K	0	1,513K	1,487K	869K	2,356K

Note: The Center for Glass Research fiscal year (and that of Alfred University) runs from July 1 to June 30, so the cost share figures reported are for time periods shifted by three months from the DOE budget periods.

State of Ohio: Improvement of Performance and Yield of Glass Fiber Drawing Technology

QUARTERLY PROGRESS REPORT

Project Title: Improvement of Performance and Yield of Glass Fiber Drawing Technology

Covering Period: July 11, 2002 through September 30, 2002

Date of Report: October 15, 2002

Recipient: State of Ohio, Office of Energy Efficiency
77 S. High Street
Columbus, OH 43215-6108

Award Number: DE-FC07-02ID14347

Subcontractors: Cleveland State University

Other Partners: PPG Industries Inc
Schott Glas

Contact(s): Dr. Phillip A. Sanger -Principal Investigator
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Project Team:
DOE-HQ Team Leader: Elliott Levine
DOE Regional Team Leader: Brian Olsen
DOE Project Manager: Matea McCray
DOE Contract Specialist: Layne Isom

Project Objective: Investigate the basic science of continuous glass fiber drawing and use that information to improve the drawing process: 1) demonstrate reduced break frequency on a state of the art fiber-drawing machine from 1 break per hour to 1 break per 4 hours, 2) reduce fiber diameter variation, 3) drive toward six-sigma* quality through process control and computer simulation.

Background: Fiber breakage is the single most important process variable in the drawing of continuous glass fibers limiting fiber quality and production throughput and resulting in over 500 10^9 BTU of energy wasted annually. Continuous glass fiber drawing in "state of the art" glass industrial facilities is accomplished in the simultaneous drawing of up to 5000 filaments from a single bushing. The perturbation caused by the breaking of one filament which

typically occurs once per hour quickly propagates toward disruption of all 5000 filaments. During the recovery time of 5-10 minutes, the glass is continuing to ooze through the bushing holes. Over 67,000 tons of unrecyclable glass annually and all the energy invested in the melting and forming of this wasted glass is lost. To address this problem, this project will apply six sigma quality methodology combined with fundamental glass science to reduce breakage, increase throughput and improve the quality of glass fiber.

Status: The subcontract to Cleveland State University was initiated on August 1, 2002. In this short first quarter, the project focussed on three of the five project tasks:

Task 1 Build and Install Glass Fiber Drawing Tower

The objective of this task is the construction of a continuous glass fiber drawing tower with a capacity of up to 400 fibers and 40 lbs per hour. This facility is central to the program and will be used to validate models and to demonstrate process improvements. Long lead items have been ordered and construction begun. The state of the art tower whose major components are being provided as cost share to the program is being assembled first at the PPG plant in Lexington, NC for later shipment to CSU late in the fourth quarter.

Task 2 Develop diagnostic Instrumentation

The development and installation of instrumentation key to the monitoring of the glass fiber drawing process is the goal of this task. The on-line dimensional characterization (primarily major and minor axis) of the fiber bundle has been identified as an important issue. No off-the-shelf technique exists for this measurement and early conceptual discussions have been initiated within our team and with potential vendors of subcomponents.

Task 3 Develop simulation models

A key element of our technical program is the identification of the key process variables of continuous glass fiber drawing and the development of the process model to used in the establishment of the transfer function between the input variables and the output performance requirements. We have begun the construction and debugging of a rapidly running model which can be used in our investigation of process variation. We expect the first cut at the models to be complete in the next quarter.

Plans for Next Quarter:

Next quarter's activities will focus on initial construction of the models, completion and prepare for shipment to CSU of the fiber drawing tower and an evaluation of potential on line process diagnostics particularly dimensional characterization of the final fiber bundle.

Patents: None

Publications/Presentations: None

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	**Build and Install Drawing Tower**			
1.1	Install tower	1/10/03		
1.2	Complete debug process	05/15/03		
1.3	Install new design of bushing	11/15/03		
2	**Develop diagnostic instrumentation**			
2.1	Install IR and high speed photo system	03/01/03		
2.2	Implement dimensional characterization process	09/15/03		
3	**Develop simulation models**			
3.1	Initiate testing of models	12/20/02		
3.2	Complete transfer function	04/16/03		
4	**Optimize process**			
4.1	Validation	07/30/03		
4.2	Demonstrate improved process	03/15/04		
5	**Disseminate technology**			
5.1	Hold first tech transfer training session	10/30/02		
5.2	Start final partner implementation	05/30/04		
6	**Final Report**	08/30/04		

Budget Data (September 30, 2002):

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	July 11, 2002	July 30, 2003	$554,014	$166,070	$720,084	$23,919	$14,466	$38,385
Year 2	August 1, 2003	July 30, 2003	$419,935	$122,525	$536,410	0	0	0
Totals			$967,899	$288,595	$1,256,494	$23,919	$14,466	$38,385

Energy Efficiency

ANL: Development and Validation of a Coupled Combustion Space/Glass Bath Furnace Simulation (Techneglas)

QUARTERLY PROGRESS REPORT

Project Title: Development/Validation of an Advanced Multiphase Glass Furnace Model

Covering Period: July 1, 2002 through September 30, 2002

Date of Report: October 29, 2002

Recipient:

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

Techneglas, Inc.
727 E. Jenkins Avenue
Columbus, OH 43207

Award Number: *DE-SC02-97CH10875 and DE-SC02-00CH11037*

Subcontractors: Mississippi State University, Purdue University

Other Partners: Libbey, Inc., Osram-Sylvania, Owens Corning, Visteon

Contact(s):

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mpetrick@anl.gov

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Project Team: *Elliot Levine, OIT DOE–HQ contact; Matea McCray,DOE-ID, Project Mentor*

Project Objective: This project is the second phase of a program to develop a "state of the art" glass furnace model which couples the combustion space to the glass melt through a rigorous spectral radiation model. The key technical objectives of this follow on program is to incorporate glass chemistry models into the glass melt, activate gaseous phase transport (bubbles/foam) in the glass melt, develop/incorporate chemistry/nucleation models to model the transport of gases/particulates emanating from the batch/molten glass into the combustion space, develop/incorporate glass quality indices, develop/validate several furnace simulations of different types of furnaces, disseminate a beta version of the code to the glass industry participants (GMIC members), and to conduct a workshop at the end of the project to transfer the technology (code) to the entire glass industry.

Background: A substantial effort has been expended during the past several decades to develop furnace models to predict furnace performance as evident by the accelerating number of publications in the literature. These efforts, in general, have had varying and limited objectives. The models developed generally have required or been based upon major underlying

assumptions that substantially impact the predictions, (such as assumed surface temperature and heat flux distributions). Also, very little experimental data has been obtained from operating furnaces which has hampered assessment of the validity of the models. The models developed thus far do not have many analytical capabilities required by the industry.

This program which was initiated in CY 1998, has been structured to develop a validated CFD furnace model that will have the desired analytical capabilities which can be used by the glass industry to define and evaluate opportunities to modify furnace operating and geometrical parameters to improve glass quality and productivity (glass throughput) while minimizing energy use and gaseous and particulate emissions. The successful development and incorporation of these models will provide the industry with a state of the art furnace model that will represent a step change in analytical capability. The ultimate utility of the state of the art model will be in the development of furnace control software to adjust operating conditions to achieve and/or maintain predetermined glass quality and furnace performance targets.

Status:

Program progress is presented in accordance with the work breakdown structures adopted for each phase of the program. Task I.# refers to a task number from the first phase while Task II.# refers to a task number from the second on-going phase. A brief summary of progress in tasks pursued during the last reporting period follows.

Task I.6: Samples of glass containing gaseous voids, prepared by Purdue University, were experimentally investigated. An analysis of the radiative characteristics of glass foams has been performed using an inverse procedure coupled with sensitivity studies to ensure the good behavior of the inversion algorithm. The transmittance, reflectance, and absorptance have been calculated using this procedure.

Task I.20: An updated version of the code (GFM2.0) was distributed to all industrial partners at the quarterly meeting in August. There has been extensive interaction between the industrial partners and ANL both before the release of the latest version of GFM2.0 and after the release. The industrial partners are currently using the code to model their selected furnace(s)

Task I.21: The industrial partners have defined the parametric studies that they will be pursing on their own furnaces using the glass furnace model. The industrial partners are working on these studies with the

assistance of ANL. It is expected that some of the results from these studies will be presented at the workshop in October.

Task I.23: Extensive preparations are underway for holding a workshop in October to disseminate the demonstration version of GFM to the GMIC members. The demonstration code was made ready by comprehensive testing and debugging

Task I.24: The de facto support center for the GFM code established at ANL (described in previous quarterly reports) has continued to function. The industrial partners have increasingly interacted with the center to obtain technical assistance in modeling their furnaces, to report bugs in the software, and to make suggestions for improving the software. Many of these suggestions have already been incorporated into the models.

Task II.2: The glass melt model now has the capability to model liquid, solid and gas phases. These models have been tested and the results (bubble distributions in the melt as a function of size) appear to conform to expectations.

Task II.3: The radiation model for the glass melt has been completed. The radiant heat fluxes were incorporated into the enthalpy source terms in the glass melt flow calculation. The calculated effect of the spectral heat fluxes on the temperature field is reasonable and the calculated change in the maximum temperature between the Rosseland approximation results and the results obtained from the spectral model agrees with results in the literature.

Task II.5: The industrial partners have compiled a list of desired glass quality indices. ANL will review this list and will incorporate several of the suggested indices into the melt model.

Task II: 6: Tests of the newly developed glass temperature probe have been performed. The probe will be used in the measurement campaign in Libbey's Toledo furnace.

Task II.8: Simulations of the Libbey, Inc. Toledo furnace have been constructed by Libbey, Inc. personnel and by staff members at ANL using the operating data from the dates when the validation measurements were taken. The results of the analysis currently underway will be compared to the in-situ measurements to further validate the GFM code.

Task II.11: During the quarter, a measurement campaign was carried out at Libbey's regenerative glass furnace in Toledo, Ohio. Measurements of wall temperatures, gas temperatures, radiation heat flux, and gas

compositions were obtained. Libbey personnel were extremely helpful in acquiring this data. The data is currently being analyzed and as indicated above will be used in validation studies.

Task II.14: The industrial partners have been actively interacting with ANL code developers to model their selected furnaces.

Plans for Next Quarter:

Work will continue on the following tasks: (1) a measurement campaign at an Owens-Corning furnace; (2) continued modeling of gas release from melt/batch to combustion space; (3) execution of the workshop to present the GFM1.0 demonstration code just before the Glass Problems Conference in Columbus, OH; (4) additional validation of the GFM by comparison with data derived from measurement campaigns; (5) continued application of the code by industry; and (6) continued refinement of melt chemistry/gas release/radiation models

Patents: The Glass Furnace Model software (GFM 1.0) was copyrighted (May 14,2001).

The Glass Furnace Model software (GFM 2.0) was copyrighted (ANL-SF-01-030b) (May 17, 2002).

Publications/Presentations: (from this quarter only)

Milestone Status Table:

ID Number	Milestone Description	Planned Completion	Actual Completion	Comments
1	**Part I**			
1.1	Select Furnace	10/1/98	10/1/98	
1.2	Combustion space simulation completed	12/1/99	10/1/99	
1.3	Glass bath simulation of furnace completed	10/1/99	10/1/99	
1.4	Verification of selected diagnostic instrumentation capabilities completed	10/1/99	10/1/99	
1.5	Combustion and glass bath simulations integrated into overall furnace studies	7/1/00	5/15/00	

ID Number	Milestone Description	Planned Completion	Actual Completion	Comments
1.6	NOx kinetic model incorporated into furnace simulation	7/1/00	4/15/00	
1.7	Preliminary validation of furnace simulation completed	10/1/00	9/15/00	
1.8	Acquisition of furnace performance data for code validation completed	5/1/01	2/20/01	
1.9	Furnace simulation validation completed	7/1/01	7/1/01	
1.10	Workshop to introduce industry to the furnace simulation software	10/1/01		Workshop to be held at the Glass Problems Conference 10/21/02
	Part II			
2.1	Reduced batch/melt chemistry/kinetic models developed	10/1/01	10/1/01	
2.2	Development of advance furnace model completed	4/1/02		Deferred at the request of industrial participants to re-orient program resources on completing GFM2.0
2.3	Simulation of selected furnace types completed	10/1/02		Will be complete in the fourth quarter of 2002
2.4	Performance data acquired from selected furnaces	2/1/03		
2.5	Validation of furnace model completed	4/1/03		
2.6	Beta sites established to test furnace model	10/1/03	11/1/01	Active
2.7	Advanced furnace model made available to industry via a workshop	12/1/03		
2.8	Support center to assist industry in the use of furnace code	12/1/03	11/1/01	Support center currently assisting project members only

Budget Data (as of 6/30/02): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods.

				Approved Spending Plan			Provided to Date	Actual Spent to Date
Phase/Year/ Budget Period				DOE Amount	Cost Share	Total	DOE Amount	DOE Amount
		From	To					
1	1	12/01/97	11/30/98	490.5	331.9	822.4	696.0	46.7
1	2	12/01/98	11/30/99	484.0	314.4	798.4	81.6	409.6
1	3	12/01/99	11/30/00	479.1	407.4	886.4	565.5	674.0
2	1	09/01/00	08/31/01	512.7	665.6	1178.4	300.0	486.9
2	2	09/30/01	09/30/02	588.7	415.9	1004.7	627.0	610.4
2	3	09/30/02	12/31/03	262.1	681.9	944.0	547.0**	
			Totals	2817.1	2817.1	5634.3	2817.1	2227.8

*Program started officially 07/31/98
**Authorized but not released due to continuing resolution

SNL: Glass Furnace Combustion and Melting Research Facility

9

Quarterly Progress Report

Project Title: Glass Furnace Combustion and Melting Research Facility

Covering Period: July 1, 2002 to September 30, 2002

Date of Report: November 22, 2002

Laboratory: Sandia National Laboratories
7011 East Avenue
Livermore, CA 94550

FWP/OTIS Number: EEW1375/ED1805000

Subcontractors: A. C. Leadbetter & Son, Inc., Toledo, OH 43607
Lilja Corp., Livermore, CA 94550
Merkle Engineers, Inc., Galena, IL 61036
Maxon Corp., Muncie, IN 47302

Other Partners: PPG Industries, Inc., Pittsburgh, PA 15238

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E-mail: rjgalla@sandia.gov

Project Team: DOE-HQ Contacts: Elliott Levine and Charles Sorrell

Industry Contact: John J. Connors
PPG Industries, Inc., Pittsburgh, PA 15238

Project Mentors: Vincent I. Henry
Henry Technology Solutions, LLC, Ann Arbor, MI 48103

John F. McConnell
JFM Consulting, Inc., Pittsburgh, PA 15220

Project Objective: The objective of the research to be done in the Melting Research Facility is to provide industry with methods for optimization of heat transfer, new sensors for combustion space conditions and glass properties, analysis of interactions between combustion product and glass compositions (e.g. -OH content and redox state), burner design concepts and testing, optimization of the location of burners and distribution of fuel, reduced emissions of NO_x and particulate, detailed data for validation of numerical models, new approaches to furnace control, testing of new batch formulations, measurements to track processes taking place during melting and fining, and control of alkali volatilization, transport, deposition on refractory, and refractory corrosion.

Background: The need for a Glass Melting Research Facility where problems common to all types of glass manufacturing can be solved is called out in the Glass Industry Technology Roadmap. Visteon Glass Systems proposed to fill this need with a melting tank furnace equipped with state-of-the-art diagnostics, located in the DOE Combustion Research Facility at Sandia National Laboratories in Livermore, CA. Input on the configuration and objectives of the

facility was sought from the entire industry through a survey distributed to industry leaders by GMIC, a workshop conducted following the OIT Glass Industry Project Review at Argonne, IL, in September 1999, discussions with numerous glass engineers, scientists, and executives, and visits to manufacturing plants and research centers. The recommendations from industry were that the tank be made large enough and flexible enough to reproduce as many as possible of the configurations and incorporate all of the important features and processes found in industrial melting furnaces. Realization of this objective, while still providing optical access for measurements in the combustion space and glass, was the principal challenge in the development of a conceptual design. An initial concept was advanced, specifying the tank area, pull rate, fuel heat input, continuous batch feed, bubblers, and optical diagnostics, and documented in a report submitted to the program manager in March 2000.

Following the reorganization of Visteon in 1998/99, the OIT Glass Team asked PPG Industries to take Visteon's place as industry lead, and PPG assumed that role in December 2000. A team of scientists and engineers from PPG, Sandia, and contractors specializing in glass manufacturing equipment was fully engaged in the design and engineering of the research facility from February to September 2001. The project participants have resolved, as a group, the principal technical questions regarding batch preparation, batch charging, furnace design, burner design and placement, refractory selection, glass circulation, and access to the furnace for measurements and sampling. Resolution of these problems has been accomplished while keeping in mind the scientific objectives of the facility as well as the need to properly represent industrial glass production conditions.

The resulting design of the research melter closely follows the most advanced industrial practice. The melting area is to be 13 ft x 6 ft, with a glass depth of 3 ft and an average height in the combustion space of 3 ft. The maximum pull rate will be 25 tons/day, ranging from 100% batch to 100% cullet. The furnace will be fired using oxygen and natural gas, will have continuous batch feed, and will be equipped with bubblers. The furnace can be fired in three modes: (1) using a single large burner mounted on the front wall, or (2) by six burners in a staggered/opposed arrangement, three in each breast wall, or (3) by a down-fired burner mounted in the crown in any combination with the front wall or breast-wall-mounted burners. Three-inch-high slots will be provided between the tank blocks and tuck stones and between the breast wall and skewback blocks, running the entire length of the furnace on both sides, to provide access to the combustion space and the surface of the glass for optical measurements and sampling probes. Vertical slots in the breast walls will provide additional access for measurements and sampling. The furnace and tank are to be fully instrumented with standard measuring devices, such as flow meters, thermocouples, continuous gas composition analyzers, optical pyrometers, and a video camera. The output from the instruments will be continuously recorded and simultaneously made available to other researchers via the Internet. The lab will be equipped with conventional and laser light sources needed for optical measurements of gas temperature and gaseous species and, using techniques to be developed in the Research Facility itself, glass temperature and glass composition. The proposed focus of the first measurement campaign is on radiative exchange among all the major emitters and absorbers in the furnace: flames, combustion products, crown, superstructure, openings, batch, foam, and clear glass. Both conventional and optical methods would be applied to measurement of temperature, composition, and radiative properties of these media.

Status:

The completed engineering packages were submitted by the furnace, batch system, and glass discharge system subcontractors on July 15. The packages were reviewed by Sandia, JFM

Consulting, and Henry Technology Solutions during a meeting at Sandia on July 18-19. The engineering of the furnace, batch handling system, and glass discharge system is now complete. All of the technical problems encountered were resolved in such a way as to maintain the essential character of the melting furnace as a research facility while conforming to glass industry practice for furnace construction and operation.

Cost estimates have been completed. Final report preparation has been delayed due to the departure of the Principal Investigator, Peter Walsh from Sandia for a faculty position at the University of Alabama.

Plans for Next Quarter: Placement of a Contract with Peter Walsh to facilitate completion of the final report. Assuming timely placement of the contract, the report will be completed by January 2003 or earlier.

Patents: none

Publications/Presentations: Project summary presented at DOE/OIT Glass Programs Review, September 2002

Milestone Status Table: Following are the tasks and schedule for completion of the present phase of the work, to arrive at a comprehensive design for the facility and an estimate of its cost.

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Completion of engineering design	7/31/02	7/15/02	
2	Completion of drawing package and facility specifications	8/31/02	7/15/02	
3	Preparation of final report	9/30/02		
4	Preparation of construction cost estimate	9/30/02	9/1/02	

Budget Data (as September 30, 2002):

			Approved Spending Plan ($000)			Actual Spent to Date ($000)		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	9/98	8/99	157	36	193	157	36[1]	193
Year 2	9/99	8/00	750	500	1,250	250	500[1]	750
Year 3	9/00	8/01	500	500	1,000	900	500[1]	1,400
Year 4	9/01	8/02	383	383	766	199	350[1]	549
Year 5	9/02	8/03	----	----	----	251[2]	----	251
Totals			1,790	1,419	3,209	1,757	1,386	3,143

[1]Sandia National Laboratories estimate

[2] Includes funds set aside for Year 5 contracts to cover completion of final report

Environmental

ANL: Development of a Process for the In-House Recovery and Recycling of Glass Manufacturing Wastes

10

Quarterly Progress Report

Project Title: Development of a Process for the In-House Recovery and Recycling of Glass From Glass-Manufacturing Waste

Covering Period: July 1st-September 30th, 2002

Date of Report: October 30, 2002

Laboratory: Argonne National Laboratory (ANL)
9700 South Cass Ave
Argonne, Illinois 60439

FWP/OTIS Number: 49014

Subcontractors: None

Industrial Partners: Saint-Gobain Vetrotex America (John Wells)
CertainTeed Corporation (Terry Berg)

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(2) Terry Berg
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E-mail: Terrl.L.Berg@saint-gobain.com

Project Objective: Develop a technology that will enable the Glass Fiber Industry to recycle its glass-fiber-forming waste and fiberglass-manufacturing scrap into new glass or into new glass products without either adversely impacting its operations due to the increasing glass-filament breakage rate, or the quality of its products.

Background: The Glass-Fiber Industry produces three solid-waste streams: glass-fiber-forming waste, fiberglass-manufacturing scrap, and fiberglass-product scrap (end-of-life scrap). The glass-fiber-forming waste is "spaghetti-like" with varying diameters and varying in lengths from a few μm to a few mm. It has a wide range of polymeric coatings or binders on the surface that are not compatible with the glass. These coatings must be removed before the glass-fiber waste can be recycled. Recycling of this waste without removing the

polymeric-coating has resulted in an increase in the number of filament breaks occurring in the glass-manufacturing process. This increased breakage rate subsequently increases the amount of waste generated. Therefore, recycling of this waste without coating removal is uneconomical and more than 50,000 metric tons of this non-biodegradable waste continues to be landfilled. The removal of the polymeric-coating layer off of the glass fibers in the waste stream, so it can be recycled, will save the glass industry substantial amounts of energy, raw materials and money. According to the document Glass: A Clear Vision for a Bright Future "… use of recycled glass actually lowers energy costs alone, by an average of $4 to $9 per metric ton compared to solely using virgin raw materials." As stated earlier, the problem in recycling the glass-fiber waste is that it is contaminated with non-compatible materials. These contaminants, in addition to the polymeric-coating layer (sizing), also include contaminants from the virgin raw materials, and contaminants in the form of tiny noble metal particles from the dies (bushings).

Fiberglass-manufacturing scrap is generated when making final products such as fiberglass insulation batting, or fiberglass-reinforced composites such as car panels. This scrap stream is also contaminated with polymeric binders that are used to make "composites" with the glass. It is estimated that the size of this scrap stream is over 165,000 metric tons a year. When these products reach the end of their useful life, they constitute over 10,000,000 metric tons of waste per year. Purification of fiberglass scrap is required before it can be recycled efficiently and economically.

The approach we took in developing a process for the removal of the polymeric-layer coating off of the glass-fiber-forming waste, involved identifying the contaminants followed by developing a technology to remove the contaminants. Environmental and economic analyses of the process were then conducted to assess its environmental acceptability and economic competitiveness. The same approach was applied for developing a process for removing the binder off of the fiberglass-manufacturing scrap, except that in this case, the only contaminant that is of concern, is the polymeric-binder.

The glass-waste recycling project started in July of 2001. The focus of our work conducted to date has been on developing a method to effectively and economically remove the polymeric binders to free the glass fibers of "incompatible contaminants". We have conducted analyses on many waste-glass samples, before and after processing, and on virgin-glass samples, to identify "foreign species" in the glass waste. At present, analyses have not shown the presence of any impurities, other than the increased carbon content due to the chemical binders used to coat the glass fibers. We have conducted experiments on two methods for removing the glass binders: thermal treatment and chemical degradation. The results we have obtained so far indicate that both of these methods can produce cleaned samples with total carbon levels reduced from several thousand ppm to less than 100 ppm, which is the level observed in the virgin "uncoated" glass samples. We also developed conceptual designs for integrating the thermal-treatment method with the glass-manufacturing process and have developed an economic analysis of the process. Additionally, we have conducted experiments on fiberglass waste using these two treatment methods. The thermal method was capable of removing over 99.5% of the binder material on the glass fibers.

Status: We completed the development and evaluation of the thermal treatment and chemical degradation methods for removing the polymeric coating off of the glass-fiber forming waste and thereby recovered glass fibers from glass-fiber forming waste. We then conducted chemical analysis of the effluent gases and vapors and conducted froth-flotation tests to remove metallic fines present in the glass fibers waste generated during the grinding of the glass fibers. We also completed the development and evaluation of the thermal treatment and chemical degradation methods for removing the polymeric binder off of the and fiberglass-manufacturing scrap to free the glass fibers of "incompatible contaminants". We attended the FY02 OIT Glass Project Review on September 10, 2002 at Sandia National Laboratories. We also started discussions with our industrial partners for conducting a large-scale test to prove the technology. The results are discussed below.

Glass-Fiber Forming Waste

Identification of Impurities: We conducted froth-flotation experiments with the sole purpose of concentrating the platinum particles from the waste stream in order to enhance its detection probability and maybe that of the other noble metals (iridium and palladium). The glass fiber waste was first shredded, some in an industrial hammer mill devise and some in a laboratory blender and the shredded materials were then combined. The shredding process introduced additional metal contaminants into the waste material as was

evidenced by the analysis later. The results showed that the concentrated fraction contained platinum, palladium and barely detected iridium. In these tests about 872 grams of shredded glass-fiber waste were subjected to froth flotation to sink the metals. We recognize that at such low metals concentrations, froth flotation may not achieve anywhere near complete separation and that 872 grams may not be a representative sample. However, it represents an improved chance for finding these species over the SEM, EDS and ICP analysis that we conducted before on much smaller samples. At the end of the experiments, the sinkers from all of the experiments were combined and the floaters were combined and analyzed by monitoring different isotopes using the ICP-MS technique. The floaters weighed about 866 grams and the sinkers weighed 4 grams after drying. About 2 grams of the starting material were lost. All of the sinkers were sent for analysis and 467 grams of the floaters were analyzed. The results are given in Table 1.

Table 1. Results of the ICP-MS Analysis of the Froth Flotation Separated Fractions

Sample ID	Sample Mass, g	Platinum mass, μg	Iridium mass, μg	Palladium mass, μg
Floaters	467	1.54 +/- 0.15	0.09 +/- 0.02	3.4*
Sinkers	4	0.19 +/- 0.02	< 0.02	(1.2)*

* The analysis for palladium was not consistent suggesting a possible interference on this element.

These results indicate that the original waste sample contained about 3.5 PPB of platinum and about 190 PPT of iridium. Recognizing that the sample may not be a representative sample, we do not consider the data to be quantitatively representative. It did, however, prove that these metals do exist in the waste-glass fibers stream. The two samples shown in Table 1 were also analyzed using the ICP-AES (atomic emission spectroscopy) technique to assess the magnitude of contamination due to shredding and to investigate if whether these new contaminants could be removed by the same froth flotation process or whether additional processing is required. The results are given in Table 2 below. The results show that, as expected, significant contamination of the glass-fiber waste samples occurred due to shredding. The results also show that all of the molybdenum, about a third of the magnesium and nickel, about half of the copper, and only 10-20% of the other elements were also removed. Obviously different froth-flotation solution conditions will be required to remove the other metals.

Table 2. Results of the ICP-AES Analysis of the Froth-Flotation Separated Fractions

Sample ID	Weight of Different Elements in Each Fraction, mg													
	Al	Ba	Ca	Cu	Cr	Fe	Pb	Mg	Mn	Mo	Ni	Sr	Ti	V
Floaters	2300	1.17	5471	0.98	8.44	114	0.56	70	0.72	<0.10	2.82	4.28	23.2	0.52
Sinkers	225	0.18	617	0.88	3.24	26.0	0.14	36	0.17	0.18	1.57	0.74	3.18	0.12
% Sunk	9	13	10	47	28	19	20	34	19	100	36	15	12	19

We also analyzed the two samples of the excess liquid that drains off the glass fiber waste. The first sample was collected from fresh waste and was supplied in a closed jar. The second sample we collected from the bottom of a 55-gallon drum in which glass fiber waste was shipped. At the time the second liquid sample was collected the material was sitting in the 55-gallon drum for about one month. The samples were analyzed by the ICP-AES technique. The results of the analysis of the two samples are summarized in Table 3. The estimated platinum concentrations in these samples are 38 PPB and 44 PPB for the Jar and drum, respectively and was determined thorough ICP-MS. These results indicate that the platinum concentration in the excess liquid is about an order of magnitude higher than in and on the glass fiber waste material itself. Once again, these results are preliminary and derived from the few samples and therefore, should be treated with care and the reported quantities may not be representative. However, it definitely supports our recommendation that washing of the glass-fiber waste with fresh water should be done before treatment to remove the polymeric-coating layer.

Table 3. Results of the ICP-MS Analysis of the Excess Liquid Samples

Sample ID	Sample Mass, g	Platinum mass, μg	Iridium mass, μg	Palladium mass, μg
Jar Sample	~800	30.3+/-3.1	0.07+/-0.02	0.15*
Drum sample	~1000	44.2+/-4.5	< 0.02	0.32*

* The analyses for palladium were not consistent suggesting a possible interference on this element.

Thermal-Treatment Method: During the previous quarter we designed and built a gas collection system, shown in Figure 1, and collected samples of the gases and vapors that evolve during the thermal treatment of

glass fibers waste to identify appropriate environmental controls. In order to identify some of the intermediates that may escape oxidation in tiny amounts in the field, we conducted the tests under reduced air-flow conditions to the thermal reactor. Obviously, the evolved gases depend on the types of materials present in the polymer coating layer. During the gas collection process we treated 214 grams of glass-fiber waste, and we estimated that we collected about 70% of the evolved gases. A total of 13.09 mg of pollutants were collected in the three collection units shown in Figure 1. The results of the chemical analysis of the gases that evolved from the glass fiber samples are given in Table 4.

Table 4. Emitted Pollutants in an Oxygen Deficient Environment From Glass Fiber Waste

Compound	Wt in mg	Wt % of Total	Compound	Wt in mg	Wt % of Total
Acetone	10,132	77	Styrene	23	0.2
Isopropyl Alcohol	1,030	08	1,2 Dichloroethane	21	0.2
Benzene	794	06	Naphthalene	20	0.2
Acrylonitrile	473	04	3-phenylfuran	15	0.1
Toluene	206	02	Xylene	12	0.1
2-Butanone	159	01	1-methyl naphthalene	10	0.1
1,1,1,2 tetrachloroethane	152	01	Others	19.5	0.1
Cyclopentanone	25	0.2	Total	13091.5	100

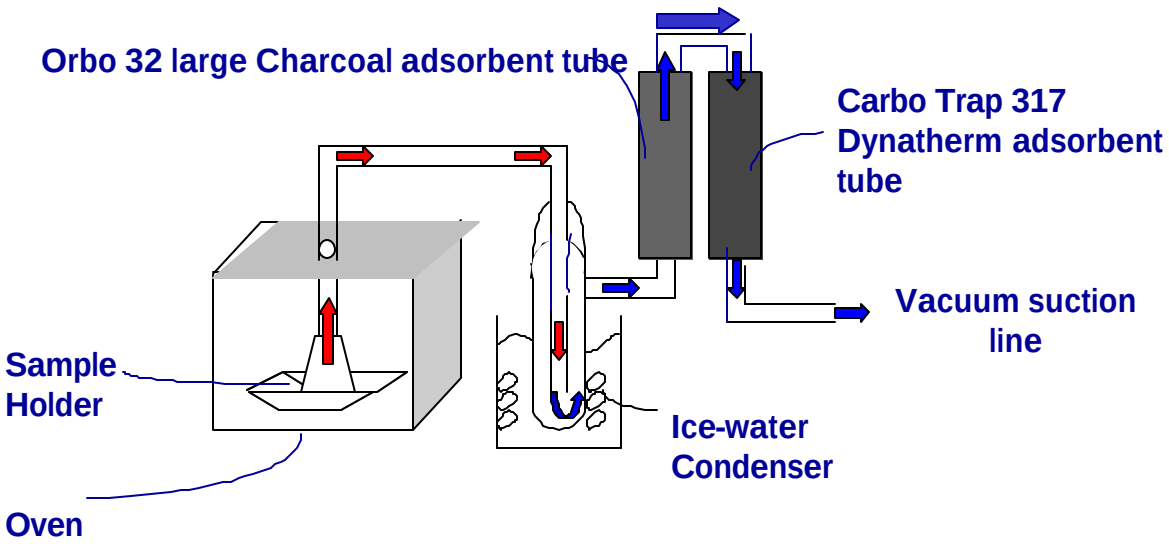

Figure 1. Gas-Sampling Subsystem

These results lead to the following observations and conclusions:

1. Based on these data we estimate that about 80 grams of gaseous emissions will escape oxidation per ton of glass-fiber waste treated. However, this should represent a worse case scenario because, as we stated earlier, in our laboratory set up we did not supply enough oxygen during the gas collection process. In actual glass manufacturing operations excess oxygen is available.
2. About 97% of the emissions are acetone, isopropyl alcohol, benzene, acrylonitrile and toluene. These should be easily oxidizable at elevated temperatures in an after burner or by mixing this gas stream with the exhaust from the melting furnace before heat recovery, if necessary.
3. The major VOCs among the evolved gases, acetone and isopropyl alcohol, will also be scrubbed by the wet scrubber included in the design that we presented in the April-June 2002 quarterly report, because they are infinitely soluble in water.

The results of the analysis were supplied to our industrial partners as part of the planning for a larger scale test. With the help of the Glass Manufacturing Industries Council (GMIC), we contacted other research institutions who are engaged in research on glass in an effort to better plan the larger scale tests.

Fiberglass Manufacturing Scrap

Thermal-Treatment Method: We also sampled and analyzed the evolved gases from the treatment of the fiberglass scrap using the gas collection system shown in Figure 1. In order to identify some of the intermediates that may escape oxidation in tiny amounts in the field, we conducted the tests under reduced air-flow conditions to the thermal reactor. During the gas collection process we treated 47 grams of fiberglass scrap, and we estimated that we collected about 50% of the gases the evolved. The fiberglass scrap lost about 7.8 grams as a result of the treatment. A total of 242 μg of pollutants were collected in the three collection units shown in Figure 1. The results are presented in Table 5.

These results lead to the following observations and conclusions:

a. Based on these data we estimate that about 10 grams of gaseous emissions will escape oxidation per ton of fiberglass scrap treated.
b. About 86% of the emissions are acetone and acrylonitrile. These should be easily oxidizable at elevated temperatures in an after burner or by mixing this gas stream with the exhaust from the melting furnace before heat recovery, if necessary.
4. The major VOC among the evolved gases, acetone, will also be scrubbed by the wet scrubber included in the design that we presented in the April-June 2002 quarterly report, because it is infinitely soluble in water.

The results of the analysis were supplied to our industrial partners as part of the planning for a larger scale test.

Table 5. Emitted Pollutants in an Oxygen Deficient Environment From Fiberglass Waste

Pollutant	Weight*, μg	% of total	Pollutant	Weight*, μg	% of total
Acetone	157	65	Diethyl ether	1	0.4
Acrylonitrile	50	21	Chloroethane	1.8	0.7
Vinyl Chloride	15	6	Chloromethane	1.5	0.6
Fimethyldifluorosilane	10	4			
Ethanol	6	3	Total	242	100

* These weights represent what was actually collected. Because we estimate that because of leaks in the system we collected about 50% of what was emitted, the actual values should be double what is given here but the percentages stay the same.

DOE Glass Project Review: We attended the DOE Glass Project Review meeting which was held on September 9-10, 2002 at Sandia National Laboratories Livermore, California.

Plans for Next Quarter: The plan for the next reporting period (7/1/02-9/30/02), is to:

(1) Conduct large-scale tests of the thermal-treatment process.
(2) Prepare a paper for publication on the treatment of Fiberglass waste with our industrial partner CertainTeed.

Patents: None.

Publications/Presentations: The following paper "A Process to Recycle Glass Fibers from Glass Manufacturing Waste" by B. J. Jody, J. A. Pomykala Jr., and E. J. Daniels, Argonne National Laboratory, and John C. Wells and Carlos E. Davis, Saint-Gobain Vetrotex America, was accepted for presentation at and publication in the proceedings of the 2003 Minerals, Metals and Materials Conference to be held in San Diego, California, on March 2-6, 2003.

Milestone Status Table

#	Milestone	Planned Completion	Actual Completion	Comments
1	Identify reason for glass-filament breakage points when recycled glass material is used	7/01	7/01	
2	Complete thermal-treatment set-up and start experiments	7/01	7/01	
3	Send thermally-treated samples to the industrial partners for characterization and analysis	8/01	10/01	
4	Complete set-up for chemical treatment and start experiments	9/01	9/01	
5	Send chemically-treated samples to the industrial partners for characterization and analysis	10/01	10/01	
6	Complete technical & economic evaluation of the thermal-treatment method	03/02	4/02	
7	Complete technical & economic evaluation of the chemical-treatment method	05/02	6/02	
8	Produce treated glass for testing by industrial partners	8/02		
9	Complete evaluation and characterization of recycled products	10/02		
10	Develop implementation/ commercialization plan & submit final report	02/03		

Budget Data

			Approved Spending Plan			Actual Spent to Date		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	7/01	9/01	200	200	400	58,966	4,374	63,340
Year 2	10/01	9/02	200	200	400	324,900	38,097	362,997
Year 3	10/03	2/03	100	100	200			

SNL/Gallo Glass Company: Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulates and Crown Corrosion

11

Quarterly Progress Report

Project Title: Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulate Emissions and Crown Refractory Corrosion in Glass Melting Furnaces

Covering Period: July 1, 2002 to September 30, 2002

Date of Report: October 31, 2002

Laboratory: Sandia National Laboratories
7011 East Avenue
Livermore, CA 94550

FWP/OTIS Number: M1ID156-HA, EEW34126, ED1805000

Subcontractors: none

Other Partners: Gallo Glass Company, 605 South Santa Cruz Avenue, Modesto, CA 95354

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Project Team: DOE-HQ Contacts: Elliott Levine

Industry Contact: John Neufeld
Gallo Glass Company, Modesto, CA 95354

Project Objectives: The objectives of the project are: (1) reduction of particulate matter emissions, (2) increase in length of furnace campaigns, and (3) improvement of melting efficiency, through simultaneous minimization of batch dust carryover, minimization of alkali volatilization, and optimization of oxygen-to-fuel ratio during glass melting and fining using wide flame oxy-fuel burners. The anticipated improvements in performance are to be achieved by reduction of alkali and particulate at its sources, reduction of unburned combustibles and waste heat losses, maximization of flame radiation through intelligent control of melting furnace conditions, and optimization of batch composition.

Background: Entrainment of batch particles in flue gas and vaporization of the alkali metals, sodium and potassium, from melting batch and molten glass are associated with a number of negative impacts on the glass melting process and melting tank performance. Among the negative effects are: (1) corrosion of superstructure and crown refractories, (2) plugging of regenerator checkers, (3) fouling and corrosion of flue ducts, (4) particulate matter emissions, and (5) loss of raw materials. The relative importance of these effects depends upon the type of glass being melted, the design and materials of construction of the furnace, and local emissions regulations. The causes of batch particle entrainment and alkali volatilization are, for the most part, well understood. However, alteration of batch composition and furnace conditions to minimize entrainment and volatilization may have negative impact on other aspects of furnace operation and glass quality. For example, volatilization could be reduced by distributing heat input so as to make the peak glass surface temperature lower and the distribution of surface temperatures more uniform, but this would suppress glass circulation in the melt and result in

poorer glass quality at a given pull rate. As another example, batch dusting could be reduced by minimizing heat input and gas velocity over the batch blanket, but the shift of fuel heat input away from the batch blanket toward the fining zone might increase batch coverage, result in poorer overall transfer of heat to the load, and would likely increase the glass surface temperature in the fining zone, leading to increased alkali volatilization and seeds in the product. Intelligent optimization of these conflicting requirements is the subject of the project. The great variability of the rates of refractory corrosion, particulate emissions, and heat requirements from furnace to furnace and the excellent performance of some furnaces suggest that an optimum set of furnace conditions exists and that significant reductions in emission and corrosion rates and improvements in the efficiencies of poorly performing furnaces are possible.

The method being used to measure carryover and volatilization is laser-induced breakdown spectroscopy (LIBS), a continuous monitoring technique for metals demonstrated in previous trials at Gallo Glass. By observing the correlation of metals concentrations with operating conditions over long periods, the batch properties and furnace conditions associated with batch carryover and alkali volatilization will be identified. Because the oxygen-to-fuel ratio is expected to be among the critical process variables, the work also includes simultaneous measurements of furnace efficiency, so that this measure of performance can be incorporated in the furnace optimization scheme.

The work has been greatly facilitated by the sooner-than-expected arrival on the market of echelle grating spectrometers, capable of recording signals from all of the elements in the LIBS spark simultaneously, permitting the identification of individual particle types and their sources or mechanisms of formation. The echelle grating instrument, originally planned for application to the problem in March 2003, was incorporated in the LIBS system during the first 5 months of the project and has been used in two sets of field trials at Gallo Glass. Though the echelle spectrometer has provided very useful data, it has not performed as well as expected. In the first round of measurements, in December 2001, the spectrometer was found not to have sufficient sensitivity for determination of element concentrations in individual laser sparks. This would preclude the determination of joint particle size-composition distributions. However, the apparent size distributions of individual elements can still be determined using the original linear spectrometer, so relatively infrequent large particles carried over from batch can be distinguished from the more uniform concentration of submicrometer particles formed from volatile species. During the most recent field test, in June 2002, both the echelle and conventional grating spectrometers were run side-by-side, for direct comparison of their performance.

Status: Two extended measurement campaigns have been conducted, in December 2001 and June 2002. Analysis of the data from the first campaign is complete; analysis of the data from the second campaign is currently progressing.

In the December 2001 measurements, flue gas composition showed cyclic variations on two time scales, one of about 12 minutes, and the other of about 1½ hours. The longer scale corresponds to the control room record of gas and oxygen flow rates; the 12-minute cycle is correlated with furnace pressure.

The indicated sodium concentration in the flue was higher during both December 2001 and June 2002 than during the 1998 tests conducted in collaboration with Corning, Gallo Glass, OIT, and Visteon. The linear spectrometer used in 1998 was brought back for comparison with the new echelle spectrometer during the June 2002 tests. Both spectrometers verified that the sodium concentrations are higher in 2001-2002 than in 1998. Comparison of the broad-

spectral-range echelle spectrometer detection system with the more traditional 30-nm window spectrometer detection system is leading to an improved understanding of both instruments.

A significant level of potassium was observed in the flue gas. The combination of potassium with sodium is expected to be a more aggressive agent for corrosion of silica refractory than sodium alone. The high measured amount of potassium is inconsistent with the chemical analysis of dust collected at the exit of the electrostatic precipitator and with the parent glass chemistry. Enrichment of potassium relative to sodium in the exhaust of glass furnaces and other combustion devices has been observed previously. The potassium concentration data are being analyzed more closely to identify the reasons for the apparent potassium enrichment.

Furnace radiative heat flux, flue gas temperature, and concentrations of oxygen, carbon monoxide, carbon dioxide, nitric oxide, and sulfur dioxide were recorded synchronously with LIBS signals during the June 2002 tests. Natural gas and oxygen input flows for the furnace were captured in strip charts from Gallo Glass. Other operating data such as furnace pressure, glass level, electric boost amount, and pyrometric wall temperatures were also obtained from Gallo Glass.

The cycles in the sodium and potassium concentrations correspond very roughly to the cycles in gas and oxygen flows (high heat input corresponds to high sodium and potassium), but the correspondence is by no means perfect. Mathematical correlation functions are currently being developed. The June 2002 data hint that an optimum furnace stoichiometry will minimize alkali concentration and avoid carbon monoxide emission. Sulfur dioxide and nitric oxide emissions are relatively insensitive to stoichiometry except under reducing conditions.

Calcium and aluminum were also observed in the flue, but at much lower concentrations than sodium and potassium. During ceramic welding, which occurred during the December 2001 field test, the aluminum concentration in the flue increased and silicon was also observed.

The apparent particle size distribution for sodium determined from the LIBS data is narrow and centered about a large particle size (several microns). This suggests a high number density of fine particles or a fume and a few large particles originating from volatilization rather than carryover.

A model for crown corrosion by sodium was developed and the values of its parameters determined from measurements during the first oxygen/gas furnace campaign on Tank No. 1 at Gallo Glass. The model provides a rational basis for assessment of the costs and benefits, with respect to refractory corrosion, from changes in operating conditions that influence sodium volatilization. An interesting prediction of the model is that when sodium reaches two or three hundred parts-per-million in the combustion space, increasing the crown temperature increases, rather than decreases, the silica corrosion rate.

Plans for Next Quarter: Work during the coming quarter will be focused on planning the next field test for early in calendar year 2003. Development of improved calibration and quantification of measurements made with the new echelle detection system will continue. Interpretation of the large quantity of data collected in June 2002 will also continue. Leadership of the project will be transferred to Linda G. Blevins of Sandia. A research/consulting contract will be established with the former Principal Investigator of this project, Peter Walsh, who has moved to the University of Alabama Birmingham.

Patents: none

Publications/Presentations: *Walsh, P.M.*, Sickafoose, S.M., Scott, D.D., Steinhaus, R., Johnsen, H.A., and Neufeld, J., "Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulate Emissions and Crown Refractory Corrosion in Glass Melting Furnaces" DOE Glass Industry Project Review, Livermore, CA, September 10, 2002.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Data acquisition system	7/31/01	6/20/02	*
2	CO and O_2 monitors	9/30/01	12/14/01	
3	Furnace exit gas temperature	10/31/01	6/20/02	
4	Flame and refractory radiation	11/30/01	6/20/02	
5	Synchronized records	12/31/01	6/20/02	*
6	Measurements of sodium	2/28/02	12/14/01	
7	Sources of sodium	3/31/02	9/30/02	
8	Conditions influencing sodium	4/30/02	9/30/02	
9	Maximum furnace efficiency	5/31/02		
10	Measurements of silicon	7/31/02	12/14/01	
11	Measurements of calcium	9/30/02	12/14/01	
12	Correlations for metals	11/30/02		
13	Broad-band LIBS instrument	3/31/03	10/31/01	
14	Software for LIBS instrument	5/31/03	10/31/01	
15	Simultaneous measurements of Na, K, Ca, and Si	7/31/03	12/14/01	
16	Relationship between Na and K	8/31/03		
17	Optimum stoichiometry	9/30/03		
18	Sodium and calcium monitor	1/31/04		
19	Control strategy	3/31/04		
20	Demo in melting research facility	4/30/04		
21	Method for monitoring and control of volatilization and carryover	5/31/04		

*It has not been possible to collect data from the control room in real time; printouts of the data acquisition system records of furnace conditions are used instead. The furnace radiation, exit gas temperature, and flue gas composition data are, however, synchronized with LIBS.

Budget Data (as of September 30, 2002)**:**

			Approved Spending Plan ($000)			Actual Spent to Date ($000)		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	6/01	5/02	350	350	700	350	350*	700
Year 2	6/02	5/03	350	350	700	145	145*	290
Year 3	6/03	5/04	350	350	700	0	0	0
Totals			1,050	1,050	2,100	495	495*	980

*Sandia National Laboratories' estimate.

Innovative Uses

Alfred University: Integrated Ion Exchange for High Strength Glass Products

Integrated Ion Exchange for High Strength Glass Products

Alfred University
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Status: A quarterly report for this project was not received by the report cut-off date. This project is still on hold, in part, due to a delay in obtaining permission to work with AFG Ind., a company controlled by Asashi Glass Co. of Japan. AFG was to provide a three-week test run in a commercial melter of the composition developed in the first phase of the project.

Work on a new proposal to resurrect this work is progressing.

PPG Industries, Inc.: Development of Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Flat Glass

Quarterly Report

Title:	Development of Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Float Glass
Covering Period:	July 1, 2002 – Sept. 30, 2002
Date:	October 30, 2002
Laboratory:	Sandia National Laboratories 7011 East Avenue Livermore, CA 94551-0969
B&R No. **FWP/OTIS:**	820101000
Subcontractors:	None
Industrial partner:	PPG Industries
Contact:	Mark D. Allendorf (925)294-2895 mdallen@sandia.gov
Project Team:	Jill Troup Glass Technology Research Center P.O. Box 11472 Pittsburgh, PA 15238-0472

Project Objectives

This project addresses the need to improve the efficiency of on-line atmospheric pressure chemical vapor deposition (APCVD) processes used primarily to deposit coatings on float glass, but also on glass containers. APCVD processes in the flat-glass industry at present can be as little as 10% efficient (i.e., only 10% of the incoming precursor chemicals are converted to coating), resulting in annual production and waste-treatment disposal costs to the industry of nearly $23 million. In addition, remelting of glass due to defects in the coatings results in over 1.1×10^{11} Btu/year of unproductive energy usage.

The objectives of this proposal are as follows:

1. Identify modifications to existing APCVD coater designs and/or new coater designs that will double the efficiency of reactant utilization, thereby substantially reducing waste emissions and purchases of raw materials.
2. Develop validated computational models to predict defects due to thickness nonuniformity and haze; use these to reduce defect frequency and improve the overall energy efficiency of the process by reducing the amount of rejected glass that must be remelted.
3. Generate a database of fundamental thermodynamic and kinetic information for APCVD.
4. Provide enhanced understanding of the underlying chemical reactions that control APCVD, which will enable the development of improved process models and control strategies for float-glass coating and other types of glass, such as containers, that use APCVD coatings.

Background:

The use of on-line atmospheric pressure chemical vapor deposition (APCVD) techniques to manufacture coatings on glass is a critical technology in the flat-glass industry, responsible for the production of approximately 110 million ft^2/year of highly value-added products. These consist primarily of low-emissivity ("low-E") and solar-control glasses for architectural applications, but also include coatings for solar cells, computer screens, automotive applications, and xerography. The markets for these products are strong and growing. Coated glass for energy-conserving windows constitutes a roughly $600 million market for the raw glass alone; the total value of the final manufactured product (primarily dual-pane glass units) is in the billions of dollars. APCVD is a virtual necessity for maximizing coating production rates, since it can be performed at atmospheric pressure and can deposit material at rates fast enough to be compatible with glass ribbons speeds on typical float lines (about 1 ft/s). APCVD is thus an economically attractive, but technologically very challenging, manufacturing process.

Status:

Project management activities

Task 1 Deposition mechanisms

- A global reaction scheme that describes the deposition of tin oxide from MBTC/oxygen mixtures was fitted to deposition-rate data obtained from the TNO continuously stirred tank reactor (CSTR). The mechanism assumes that the rate-limiting step is the reaction of MBTC with oxygen in the gas phase. Next quarter we will determine whether the mechanism can be fitted to data obtained from the PPG pilot-scale coater. If so, the results will provide a starting point to develop optimization strategies for tin oxide coating processes.

- Efforts to obtain a detailed mechanism for MBTC pyrolysis continued this quarter. The detailed mechanism used to model flow-reactor data last quarter was applied to the one-atmosphere pyrolysis data obtained in the TNO CSTR. Relatively small modifications were required to only two rate constants in order to adapt the mechanism to the higher-pressure data. The results suggest that the elementary chemistry in the mechanism is basically right and that some fine tuning should yield a mechanism that is robust enough to predict MBTC decomposition across a range of conditions.

- A manuscript describing the MBTC flow-reactor experiments was prepared and submitted for publication in the proceedings volume of the Fourth International Conference on Coatings on Glass, to be held in Braunschweig, Germany in November.

Task 2 Gas-phase and surface chemistry measurements

- No additional experiments were conducted under this task this quarter. However, the new stagnation-flow reactor is now on line (see task 4 below), which will provide a "wall-less" environment for measuring both deposition kinetics and gas-phase reaction rates. Data from this reactor should be available next quarter.

Task 3 On-line monitoring

- The GC/mass spectrometer that will be used as a testbed for developing and on-line monitoring technique is now operational. Measurements using the system will commence next quarter.

- A second GC (gas chromatograph) is being installed on the pilot-scale coating reactor located at PPG's Glass Technology Center.

Task 4 CFD modeling

- A series of calculations were performed to simulate the deposition profile in the PPG pilot-scale coater, using the deposition kinetics obtained by TNO in the CSTR reactor. The fit yields a deposition profile that is qualitatively similar to deposition-rate profiles obtained by PPG in the pilot-scale coater, but the deposition rate is too low. Discussions are underway to identify the source of this disagreement.

Task 5 Deposition experiments

- Assembly of the new optically accessible stagnation-flow reactor (SFR) is complete. Calibration of the MBTC delivery system, FTIR, and substrate heating subsystems was conducted this quarter and will be completed early next quarter. Preliminary deposition experiments show that tin oxide films can be formed from MBTC/oxygen mixtures.

- The matrix of tin oxide deposition experiments using MBTC/oxygen/water mixtures was completed this quarter on the PPG pilot scale coater. Accurate temperature profiles were also completed. The complete data sets were delivered to Sandia for use in the CFD modeling task (Task 4) and are currently being analyzed.

Task 6 Process optimization

- Modifications to the PPG pilot-scale coater to allow the glass substrate to be continuously heated while it is underneath the reactant injectors are almost complete. Glass temperature studies showed temperature gradients larger than desired. Modification of the heater to decrease the temperature gradients is in progress. Experiments using the modified reactor will commence next quarter.

Plans for Next Quarter:

The following activities are planned for next quarter:

- Complete temperature profiles in HTFR required to finish analysis of MBTC pyrolysis and oxidation data.
- Complete calibration of FTIR diagnostic and temperature calibration for SFR.
- Extract kinetics of tin oxide deposition using MBTC/oxygen mixtures from matrix of pilot-scale data obtained at PPG. Use results in conjunction with preliminary global mechanism to predict deposition profiles in pilot-scale reactor using CFD code.
- Initiate measurements of tin oxide deposition rates from MBTC/oxygen mixtures in SFR.
- Complete first phase of deposition experiments in modified pilot-scale reactor at PPG.

Patents: None this quarter.

Publications/Presentations:
Mark D. Allendorf, Anthony H. McDaniel, and Ton A. M. B. Van Mol "Decomposition of Monobutyltintrichloride in a High Temperature Flow Reactor: Rate Constants and Product Formation," accepted for publication in Proc. Fourth Int. Conf. Coatings on Glass."

Milestone Status Table:

Task	Task/Milestone Description	Completion Date		Comments
		Planned	Actual	
1.1	Develop thermodynamic data base	9	12	
1.2	Gas-phase model development	24		
1.3	Surface model development	24		
1.4	Mechanism testing/validation	24		
1.5	Chlorine defect model	24		
2.1	Gas-phase rates	18		Preliminary analysis complete
2.2	Gas-phase intermediates	24		
3.1	Equipment modification/calibration	18	18	
3.2	On-line monitoring in PPG facility	36		
4.1	Non-reacting model: pilot-scale	6	6	
4.2	Reacting model: pilot scale	18		Completion expected Month 22
4.3	Non-reacting model: full-scale	24		
4.4	Reacting model: full-scale	36		
5.1	Pilot-scale deposition experiments: Phase 1	9	15	
5.2	Pilot-scale deposition experiments: Phase 2	21		
5.3	Surface Raman experiments	18		Postponed until FTIR/GC-MS experiments completed
6.1	SFR tests	24		
6.2	Pilot-scale tests	27		
6.3	Full-scale tests	35		
	Final report	37		

Budget Data (in thousands of $)

			Approved Spending Plan			Actual Spent to Date*		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	3/01	2/02	500	500	1,000	538	394	932
Year 2	3/02	9/02	500	500	1,000	391	248	639
Year 3	3/03	2/04						
		Totals	1,000	1,000	2,000	929	642	1571

Note: project year (March – Feb) does not coincide with DOE fiscal year (Oct – Sept).